

LAPPEENRANTA-LAHTI UNIVERSITY OF TECHNOLOGY LUT  
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**PRE-TREATMENT REQUIREMENTS FOR CHALLENGING WASTEWATER  
STREAMS FROM NEW BIOCHEMICAL PROCESS TO ENABLE AEROBIC  
TREATMENT**

Examiners: Professor Mari Kallioinen  
Master of Science Marjukka Joutsimo, UPM R&D

## ABSTRACT

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### **Pre-treatment requirements for challenging wastewater streams from new biochemical process to enable aerobic treatment**

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Wood can be converted into various sustainable products such as biofuels and biochemicals. The investment cost of new biorefinery can be reduced by utilizing common services like wastewater treatment thus lowering the threshold for market entry. Treatment and discharge of industrial wastewaters are strictly controlled by native legal requirements. Their goal is to ensure good treatment performance and water quality in receiving waters. Especially wastewaters with recalcitrant or toxic characteristics need pre-treatment before discharge to centralized wastewater treatment plant utilizing biological degradation.

In this master's thesis, pre-treatment need for becoming biorefinery wastewaters originating from new biochemical processes was evaluated. The main focus was in the removability of wood-based organic compounds responsible for high COD load to the treatment plant. Evaluation was based on local and case-specific requirements and limitations, and biodegradability tests. Biodegradability was determined by COD fractionation and toxicity measurements using OxiTop BOD measurement setup. For wood handling stream, removal of solid and colloidal fractions was found to be an important pre-treatment step to achieve required treatment results. Remaining soluble contaminants had readily biodegradable nature. It is still uncertain how efficiently the existing primary treatment in the Chemical Site removes solids from these new streams. Another studied stream contained more soluble non-biodegradable COD. Application of advanced oxidation process could be a cost-efficient method for partial oxidation of recalcitrant compounds. Pilot-scale non-thermal gas phase pulsed corona discharge (PCD) was tested as an oxidation pre-treatment method to enhance biodegradability of streams. Improvements in the BOD<sub>5</sub>/COD ratio was not achieved. However, observations in color and pH change and lignin concentration results indicated that partial oxidation had occurred, which could help the following biological treatment. This was detected as decrease in conjugated structures and increase in concentration of degradation compounds like oxalic and formic acids. Optimal energy dose for sufficient pre-treatment could not be determined on the basis of these results alone. The biggest risks associated with these wastewaters and their treatment were defined as uncertainties in startup, high sulfate concentration and foaming potential.

# TIIVISTELMÄ

Lappeenrannan-Lahden teknillinen yliopisto LUT  
School of Engineering Science  
Kemiantekniikan koulutusohjelma

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## Uuden biokemikaaliprosessin jätevesivirtojen esikäsittelyvaatimukset mahdollistaen aerobisen käsittelyn

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Puusta voidaan valmistaa erilaisia kestävästä kehitystä edistäviä biotuotteita kuten biopolttoaineita ja biokemikaaleja. Uuden biojalostamon investointikustannuksia ja kynnystä päästä markkinoille voidaan alentaa hyödyntämällä yleisiä palveluita kuten jäteveden käsittelyä. Teollisten jätevesien käsittelyä ja päästöjä valvotaan tiukasti erilaisilla lakivaatimuksilla ja päästörajoilla. Niiden tavoite on varmistaa hyvä puhdistustehokkuus ja veden laatu. Erityisesti haitalliset jätevedet, joissa on myrkyllisiä ja biologisesti huonosti hajoavia yhdisteitä, tarvitsevat esikäsittelyä ennen kuin ne voidaan laskea biologiseen jätevedenpuhdistamoon.

Tässä diplomityössä arvioitiin uuden biojalostamon jätevesijakeiden esikäsittelyvaatimuksia ja tarvetta. Pääpaino oli biokemikaaliprosesseista syntyvien jätevesijakeiden sisältämien puuperäisten orgaanisten yhdisteiden poistamisessa. Ne aiheuttavat suuren COD kuorman puhdistamolle. Arviointi perustui paikallisiin ja tapauskohtaisiin rajoituksiin sekä biohajoavuustesteihin. Biohajoavuus määritettiin COD fraktioinnilla ja toksisuusmittauksilla, jotka tehtiin OxiTop BOD-mittaussysteemillä. Puunkäsittelystä peräisin olevan jätevesijakeen esikäsittelyssä tärkeää todettiin olevan kiinteän ja kolloidisen fraktion poistaminen. Liukoinen fraktio oli helposti biohajoava aerobisessa käsittelyssä. On vielä epävarmaa, kuinka tehokkaasti kemianteollisuusalueella jo olemassa oleva primaarivaihe poistaa kiintoainetta näistä uusista jakeista. Toinen analysoitu virta sisälsi enemmän liukoista ei-biohajoavaa COD:tä. Kehittyneen hapetusprosessin käyttö voisi olla kustannustehokas vaihtoehto tällaisten yhdisteiden pilkkomiseksi. Jätevesijakeiden biohajoavuuden parantamiseen testattiin pilottimittakaavassa kaasufaasipulssiin perustuvaa koronapurkausta (PCD) hapettavana esikäsittelymenetelmänä. Jäteveden BOD<sub>5</sub>/COD suhteessa ei saavutettu parannusta. Muutokset jätevesien värissä, pH:ssa ja ligniinipitoisuudessa osoittivat kuitenkin, että osittaista hapetusta on tapahtunut, mikä voisi auttaa seuraavaa biologista käsittelyä. Tapahtuneet hapetusreaktiot havaittiin konjugoituneiden rakenteiden vähentymisenä sekä hajoamistuotteiden, kuten oksaali- ja muurahaisapon, konsentraation kasvuna. Optimaalista energia-annosta riittävää esikäsittelyä varten sekä sopivaa toteutustapaa ei voitu määrittää pelkästään tässä työssä saatujen tulosten perusteella. Suurimmiksi näihin jätevesiin ja niiden käsittelyyn liittyviksi riskitekijöiksi määriteltiin startupin aiheuttaman epävarmuudet, korkea sulfaattipitoisuus sekä vaahtoamispotentiaali.

## **PREFACE**

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APPENDIX II: Toxicity measurements

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**LIST OF APPREVIATIONS**

AOX	Halogenated organic compounds
AOPs	Advanced oxidation processes
ASP	Activated sludge process
ATU	N-Allylthiourea
BAT	Best available technique
BOD	Biochemical oxygen demand
BREF	BAT reference document
COD	Chemical oxygen demand
DO	Dissolved oxygen
EQS	Environmental quality standards
EU	European Union
TOC	Total organic carbon
F/M	Food to microorganism ratio
HMW	High molecular weight compounds, >2 kDa
IED	Industrial emission directive
LMW	Low molecular weight compounds, <2 kDa
MEG	Monoethylene glycol
NERC	UPM Northern European Research Center
PCD	Pulsed corona discharge
UF	Ultrafiltration
ZAB	Centralized wastewater treatment plant in Leuna Chemical Site

## 1 INTRODUCTION

Sustainability and environmental friendliness are values that are emphasized more and more in corporate strategies. Water, as one of the major resources considering sustainability (Galanakis&Agrafioti, 2019), has gained a lot of attention due to its scarcity and contamination. United nations (2015) has set clean water and sanitation as the sixth Sustainable Development Goal. Industrial wastewaters and toxic, emerging or accumulating substances are major concerns for wastewater treatment and receiving waters. This puts pressure on treatment plants, especially for conventional and centralized treatment plants to achieve and maintain good treatment results. (EEA, 2018) Stricter regulation and increasing demand for recycling and reuse of water have driven organizations to develop and optimize sustainable technologies and solutions for water management. The difficulty of such task is related with lower energy consumption, cost and reduced discharges. (Galanakis&Agrafioti, 2019)

Another sign of increasing popularity of sustainability is the growing demand for materials from renewable raw materials. Wood-originated lignocellulosic biomass is high potential raw material for production of fuels and chemicals. UPM's new-to-the-world biorefinery located in Chemical Site Leuna, Germany, will enter the market according to the plan from 2022 onwards. Renewable glycols and lignin-based functional fillers are produced to replace fossil-based alternative products thereby enabling CO<sub>2</sub> footprint reduction in various consumer-driven end-uses. (UPM, 2020) The investment is new to UPM and its biochemicals business, since it expands the wood usage into biochemicals on an industrial scale. Wastewaters generated in the facility are treated in the industrial park's centralized wastewater treatment plant (ZAB) jointly with other chemical industry wastewaters. Such opportunity enables decrease in total capital expenditures of the new investment.

Forest industry wastewaters and their treatment has been studied widely. With new biochemical processes, the features and content of wastewaters are different and flows are much smaller compared to pulp and paper mill effluents. Also, the legislation is different for chemical and pulp and paper industries which is already a challenge for wastewaters, which contain high loads of wood-based organic compounds. Further, these kinds of wood-based streams have not been treated before in the existing biological treatment plant. The

increasing flow, high amount of organic matter and recalcitrant compounds are concerns relating to the efficiency and adequacy of the biological treatment for new effluents. Plant will be upgraded with an anaerobic treatment stage, but not all streams are suitable for biogas production due to inhibiting property or low anaerobic biodegradability and biogas yield.

The objective of this thesis is to evaluate sufficient treatment of new wastewater streams from the biochemical processes within the legal framework. In the literature part important legal requirements for this biorefinery case are set out. An overview of aerobic treatment performance, measurement of biodegradability and features of wastewater streams are presented. Pre-treatment possibilities for slowly biodegradable, recalcitrant or toxic streams are also reviewed. In the experimental part the COD composition of samples representing specific streams are determined. Aerobic biodegradability and treatability are studied. Partial oxidation with pulsed corona discharge treatment is tested to enhance biodegradability. Finally, risk assessment of the biorefinery wastewaters for InfraLeuna ZAB is compiled.

## **LITERATURE PART**

### **2 LEGISLATIVE FRAMEWORK FOR BIOCHEMICAL WASTEWATERS**

Industrial operation and pollution are controlled with legislation at different levels and varies by industry. European Union (EU) has set several directives concerning environmental pollution and waste management which must be compiled in its membership countries. The Industrial Emissions Directive (IED) 2010/75/EU, also known as integrated pollution prevention and control (IPPC), is the fundamental framework for regulating pollution to all media from industries. IED outlines permitting rules for operations potential to high pollution risk, such as pulp and paper mills or chemicals production. Also, the use of best available techniques (BAT) in the activities is introduced. BAT refers to an effective technique with low environmental impact and economic applications on real scale. Information about BAT for separate industrial sectors are gathered in BAT Reference Documents (BREF). (EUR-lex, 2015)

The protection of all water bodies within the EU region leans on the Water Framework Directive (WFD) 2000/60/EC and the Urban Waste Water Treatment Directive 91/271/EEC.

The basis for gaining good-quality water are compiled in it. Other related directives are 2006/118/EC, 2007/60/EC and 2008/105/EC which focus on groundwater pollution by high-risk substances like nitrates, pesticides and heavy metals, flood management and environmental quality standards (EQS), respectively. EQS are applicable in surface waters for priority substances and other contaminants, most of them halogenated organics and (poly)aromatics used as solvents, precursors, flame retardants, insecticides or pesticides. Together with IED, the amended directives list 57 water polluting or hazardous substances with a concentration limit. A watchlist for toxins under review is also maintained (latest Implementing Decision (EU 2018/840) and the fit for purpose of these directives was revised in 2019. (EUR-lex, 2017) Next ambition regarding the pollution prevention is the European Green Deal, which includes zero pollution action plan (European Commission, 2019).

## **2.1 German Waste Water Ordinance**

Despite the common rules in EU, discharge limits can differ at national level. In Germany, Federal Ministry for the Environment, Nature Conservation and Nuclear Safety has set the Ordinance on Requirements for the Discharge of Waste Water into waters. It is applied to relevant parameters when granting a permit to discharge wastewaters into water bodies. Minimum requirements for 57 different source categories are compiled in its appendices. The common part lists definition of used terms and applicable standard analysis and measurement procedures. The point that must comply the requirements can refer to a point prior to blending or discharge of wastewater i.e. outlet of effluent in production site or wastewater treatment plant. (BGBl. I, 2004)

The general requirements presented in Article 3 state that the permit is not granted unless the pollutant load is not minimized with the conditions in the origin of wastewater. It also states that dilution and transferring the environmental pollution to air or soil are not acceptable ways to meet the requirements. Rules for allowed blending of wastewaters from different origins specify that the separate or production site specific requirements must still be achieved in the joint treatment. If the requirements differ, a calculated limit can be derived for the individual wastewater. Requirements pursuant in this ordinance doesn't affect to more advanced legal regulations. (BGBl. I, 2004)

UPM's coming biorefinery wastewaters lands on the scope of chemical industry, which is not familiar to the company before as a production wise. Appendix 22 of the Ordinance concerns chemical industry. It is applicable for discharges over 10 m<sup>3</sup>/d that are generated by chemical, biochemical or physical techniques for production of substances. The general requirements described in part B aim to gain as low contaminant load as possible on production site. This means that used techniques should be water-saving or water-free and processes should apply indirect cooling and recirculation. To comply with requirements, used materials should be low-pollutant and substance retention and recovery techniques should be optimized. (BGBl. I, 2004)

If wastewater is mixed with other wastewater before treatment, there are specified requirements in part D which must be compiled before it is allowed. These includes limits for substances such as adsorbable organically bound halogens (AOX), few heavy metals and total organic carbon (TOC) in some cases. AOX limits are specified by production of target organic product, but there is no own limit for the production of bioglycols, lignin products or sugars. Heavy metal concentrations are reported in two levels. The upper limit applies if the particular substance participates in the process as an acting component. The stricter limit applies if the stream is otherwise contaminated with the substance. (BGBl. I, 2004) The different requirements are presented in Table I.

**Table I** Requirements before mixing with other wastewater (BGBl. I, 2004).

<b>Substance</b>	<b>Occasion</b>	<b>Requirement</b>
<b>AOX</b>	Contaminated between 0.1 – 1 mg/L	0.3 mg/L
	Contaminated above 1 mg/L	1 mg/L or 20 g/t
<b>Mercury</b>	Contaminated below 0.05 mg/L	0.001 mg/L
<b>Cadmium</b>	Contaminated below 0.2 mg/L	0.005 mg/L
<b>Copper</b>	Contaminated below 0.5 mg/L	0.1 mg/L
<b>Nickel</b>	Contaminated below 0.5 mg/L	0.05 mg/L
<b>Lead</b>	Contaminated below 0.5 mg/L	0.05 mg/L
<b>Chromium, total</b>	Contaminated below 0.5 mg/L	0.05 mg/L
<b>Zinc</b>	Contaminated below 2 mg/L	0.2 mg/L
<b>Tin</b>	Contaminated below 2 mg/L	0.2 mg/L
<b>TOC</b>	Residual discharge over 20 kg/d, 300 kg/a or 1 kg/t of production capacity	80% reduction

TOC eliminability of biological treatment plant is justified with ultimate biodegradation study according to DIN EN 9888, which can be based also on determination of COD (BGBl. I, 2004). In Germany, some COD regulations have been replaced with TOC. The change of analysis reduces costs and generation of hazardous dichromate waste from the COD measurement is avoided. COD/TOC ratios are however very case-specific and use of specific converting factor needs verifying. Ratio varies even theoretically for organic compounds and surely for wastewater treatment plant effluents from 1.7 to 6.4. In the study for chemical industry, the ratio was 2.5-3.5 with a median of 2.9. (Brinkmann *et al.*, 2016)

The final requirements at the discharge point to receiving waters are specified in part C separately for each parameter: COD, total nitrogen as sum of ammonium, nitrate and nitrite nitrogen, total phosphorus and toxicity. Limitation of the concentration of these substances is important due to prevention of oxygen depletion and eutrophication and preservation of healthy aquatic ecosystem in natural reservoirs. Inorganic nitrogen has higher acute contribution to eutrophication compared to organically bound nitrogen (Brinkmann *et al.*, 2016). Discharge limits for COD are divided into four categories based on the initial COD concentration. For pulp and paper industries, COD limit is based on the tonnes produced. (BGBl. I, 2004) The different occasions and limits are presented in Table II.

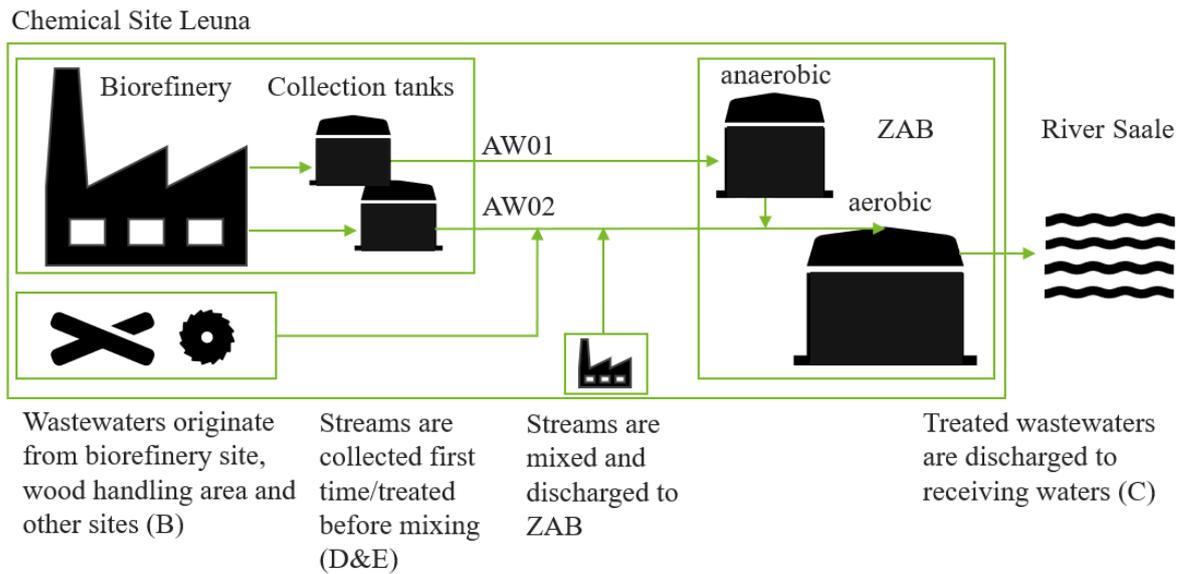
**Table II** Requirements at the discharge point for different occasions (BGBl. I, 2004).

<b>Substance</b>	<b>Occasion</b>	<b>Requirement</b>
<b>COD</b>	<75 mg/L	-
	<750 mg/L	75 mg/L
	>750 mg/L	90% reduction
	>50 000 mg/L	2 500 mg/L
<b>Inorganic nitrogen</b>		50 mg/L
<b>Total phosphorus</b>		2 mg/L
<b>Toxicity</b>	Fish eggs GEi	2
	Daphnia GD	8
	Algae GA	16
	Luminescent bacteria GL	32
	Genetic mutant potential (umu) GM	1.5

## 2.2 Case-specific wastewater permitting

All wastewaters related to UPM's biorefinery and surrounded chemical industry are treated collectively in the Chemical Site's treatment plant. This can be described as a case where UPM's wastewaters are indirectly released to receiving waters by the independently operated wastewater treatment plant. The plant and the facilities operating in the area have their own environmental permits. Biorefinery's permit must include approval for indirect discharge according to the authoritative state law. The state of Saxony-Anhalt has Indirect discharge regulation (IndEinlVO) related to their Water Act (GVBl. LSA, 2007) which is applied in Leuna. The new biorefinery will also affect the industrial park's environmental permit. In order the site altogether need to meet at least the legislative requirements presented in Table II, it sets some additional limits like maximum daily discharges to the treatment plant for each mill or factory. These take over standards of the ZAB need to be fulfilled in addition to statutory rules.

Figure 1 illustrates the permitting case. Each box represents the scope of a single permit. Letters B, D, E and C correspond to legislative points of origin of wastewater, before mixing, site of occurrence and discharge, respectively. Two streams, AW01 to anaerobic treatment and AW02 to aerobic treatment, are originated from the biorefinery, one stream is originated from the wood handling area and one stream describes jointly other production sites. Other sectors in the site are production of e.g. oil, rubber, plastics, pharmaceuticals and fertilizer products. Streams AW01 and AW02 must comply by the requirements before mixing with other wastewater and discharge to public treatment plant (ZAB) according to Table I. Requirements are monitored from qualified or 2-hour mixed samples (BGBl. I, 2004). Wastewaters from the wood handling area are not part of the biorefinery's permit and scope of chemical industry regulation.

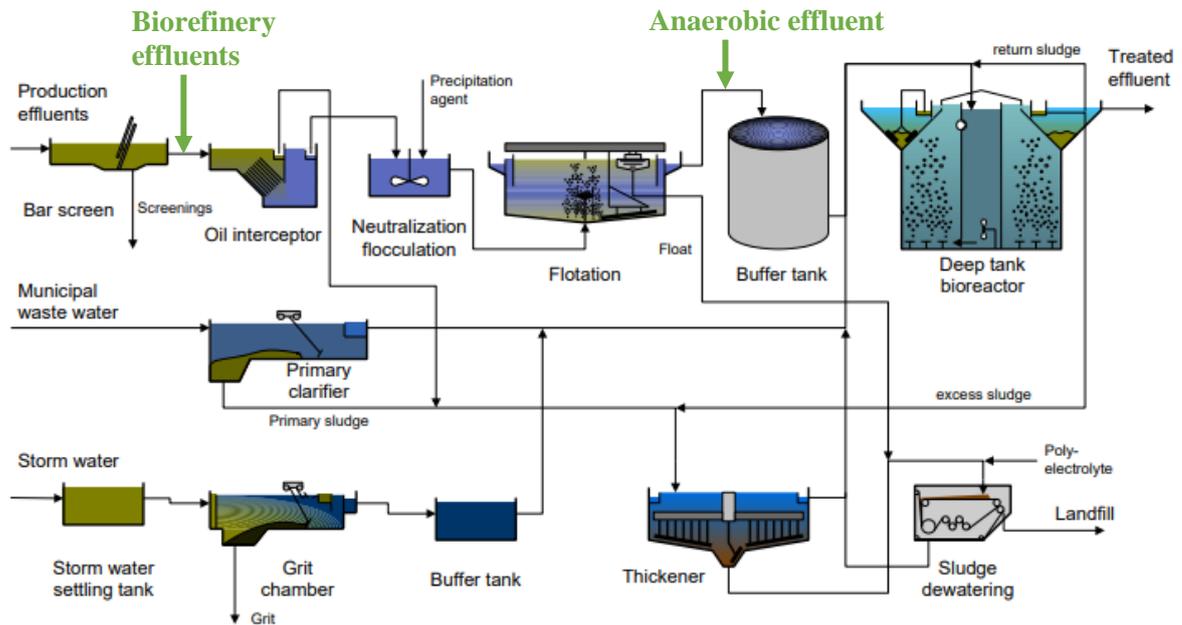


**Figure 1** Illustration and description of sewage flows at different points according to ordinance and environmental permit.

### 3 EXISTING AEROBIC TREATMENT PLANT

Aerobic treatment utilizes natural biological degradation for purification purposes. Since the development of the conventional format called activated sludge process (ASP) in 1913 and improvements in system configurations afterwards, aerobic treatment is a common method nowadays both sewage and industrial wastewater (Tilley, 2011; Tchobanoglous *et al.*, 2003). Reasons for such popularity are relatively low cost, simplicity and effectiveness in organic matter removal (Tchobanoglous *et al.*, 2003).

Typical aerobic wastewater treatment process consists of required pre-treatment stages, primary treatment for suspended solids removal, secondary biological treatment and additional tertiary (polishing) treatment for removal of residual contaminants (Tchobanoglous *et al.*, 2003). Figure 2 presents the flowchart of InfraLeuna wastewater treatment plant and discharge points of new streams to plant. Treatment plant has been designed originally for refinery effluents and municipal wastewater (Bamag, 2003). Purposes of applied pre-treatments are to separate large solids, oil, grease and foam and neutralize the pH. Otherwise harm for biological treatment would occur by equipment failure or slowing down the process. (Tchobanoglous *et al.*, 2003)



**Figure 2** Plant portrait of ZAB Leuna (modified by Bamag, 2003)

Flocculation and flotation are the primary treatment stages in which chemically precipitated flocs are aggregated and then floated by small gas bubbles. Sludge rising to the surface is removed by skimming. Removal of total suspended solids (TSS) is typically high, even 90-98% but it depends on the type of removed solids (Brinkmann *et al.*, 2016). Solids content of the sludge is 1-3% and it may be difficult to mix with other sludge and dewater. Flotation is suitable for solids with poor settleability and it requires relatively small space although it has high energy consumption and operating costs, because the air saturated water must be generated under pressure. Sedimentation or filtration are also common as primary treatment. (Hynninen, 2008)

The wastewater flows through the buffer tank into the secondary treatment, where the actual biological processes occur in aerobic deep tank bioreactor. The reactor type in ZAB is similar in principle to typical conventional suspended growth reactor, where biomass i.e. activated sludge grows and moves freely. Denitrification (anoxic) and nitrification (aerated) zones are integrated into the reactor (Bamag, 2003). Other suspended growth reactor types include sequencing batch reactor (SBR) and membrane bioreactor (MBR). Instead, reactors where the growth of biomass is attached to a natural or artificial media are called fixed-film or attached growth reactors. Typical examples of these are trickling filters, discs and moving

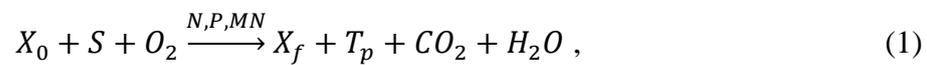
bed biofilm reactors (MBBR). Advantages in suspended growth over fixed-film reactors are better removal of nutrients, flexibility and response to inhibitors or toxins and lower residual sludge formation. On the other hand, fixed-films may be simpler to operate and require less space. In addition, a combination of both growth ways is taken advantage in integrated fixed-film activated sludge (IFAS) process. (Tchobanoglous *et al.*, 2003)

Secondary settler, in which gravitational separation and suction scrapers are applied to remove settled biomass, is integrated into the ZAB's bioreactor (Bamag, 2003). Depending on the biological phase and settling properties, 99% of suspended solids can be removed from the effluent (Tchobanoglous *et al.*, 2003). The secondary sludge is partly circulated back to aeration as recycled activated sludge (RAS). The amount of RAS depends on the operating principle of the plant, mainly the rate of sludge formation and maintained sludge age. Waste activated sludge (WAS) is removed from the process. Sludge handling for primary and secondary sludges includes thickening, dewatering and further sludge treatment such as conditioning. (Davies, 2005) Amount of solids must be under special attention in industrial wastewaters. Costs of industrial sludge treatment have risen recently, partly because dewatering is challenging due to intracellular water in the biomass. (Finnish Water Utilities Association, 2018).

The clarified effluent, depending on its quality, destination and set regulation, can be treated further on to remove residual contaminants. Physical or chemical methods or additional biological steps for example enhanced nitrogen removal and after oxidation, can be used according to need. These methods can be disinfection or oxidation by chlorination or ozonation to remove pathogens or other separation methods like ion exchange, adsorption, flotation or membrane filtration. (Hubbe *et al.*, 2016) No tertiary treatment was originally designed to the ZAB. However, improved detection capability, changing nature of wastewater and new regulations may bring about the need for enhance removal of contaminants by retrofitting or upgrading existing treatment plants (Tchobanoglous *et al.*, 2003).

### 3.1 Biological basics of pollutant removal

In secondary treatment dissolved and colloidal organic matter are removed by digestion. Aerobic microorganisms, a mixed community of mainly bacteria, but also protozoa, fungi, rotifers, amoebas and algae, consume organic matter together with nutrients nitrogen (N) and phosphorus (P) and oxygen (O<sub>2</sub>) as their energy and supply for metabolism. (Tchobanoglous *et al.*, 2003) Basically, the soluble organics from wastewater are converted into water (H<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), other simple molecules and new cells which can be described with equation (1):



where

$X_0$	initial biomass
$S$	organic carbon sources
$MN$	mineral nutrients
$X_f$	final biomass
$T_p$	transformation products of biodegradation.

Degradation happens by three major processes involving ingestion, respiration and growth. Enzymes secreted by bacteria play an important role enabling ingestion by breaking down the organics into smaller compounds. This process can take several hours to days for large complex compounds. Monomers and compounds less than 1 kDa are more easily usable as such and removed quickly. (Davies, 2005) In addition to molecular size, hydrophobicity and sorption into solids affect the bioavailability (Saski, 1998). In aerobic respiration oxygen is used as the electron acceptor to oxidize ingested compounds, producing energy required in metabolic reactions. Energy and carbon source are used by the bacteria to grow until it divides. That way the number of cells can increase exponentially till maximum growth rate is reached. (Davies, 2005)

Heterotrophic a.k.a. carbonaceous bacteria are those which use the organic carbon as their food supply. They are more fast-growing and abundant in treatment plants than autotrophs, which take in inorganics and have an important role in nitrogen transformation. Appearance of bacterial types may vary from spherical, rod shape, spiral form (size 0.5-2 μm) to

filamentous (length 100  $\mu\text{m}$ ). Heterotrophic bacteria produce extracellular biopolymers to form porous flocs (size 50-200  $\mu\text{m}$ ) in which microbes, large molecules, colloids and fine particulates adsorb and entangle to. Protozoa, rotifers and other higher trophic microbes living outside the floc consume free bacteria and particulates aiding effluent clarification. (Davies, 2005) Understanding the microbial population and distribution of its diversity in individual plants is reasonable, because microorganisms can be a good indicator on the prevailing and coming treatment and operating conditions and effluent quality (Tchobanoglous *et al.*, 2003).

Optimal environment for microbial growth and wastewater treatment is based on temperature, pH, oxygen supply and nutrients N and P balance. Typical mesophilic bacteria function best at 25-40 °C and generally, a neutral pH between 6.5 and 7.5 is desirable. In aerobic treatment, added oxygen supply can accelerate the process. Oxygen concentration as dissolved oxygen (DO) is to be kept preferably near 2 mg/L. Suitable balance for biological oxygen demand and nutrients as BOD:N:P ratio is between 100:10:1 and 100:5:1. Also, trace amounts of mineral nutrients such as sodium, calcium, magnesium, potassium and iron are required. (Tchobanoglous *et al.*, 2003)

In addition to carbonaceous treatment, biological nutrient removal is feasible. Nitrogen is removed by nitrification and denitrification steps, which are more easily inhibited by environmental variables and toxins than biosynthesis of heterotrophies. In nitrification ammonium is converted to nitrite and further on to nitrate. Denitrification includes nitrate reduction to nitric and nitrous oxides and further to nitrogen gas, which can leave the system. Biological phosphorus removal is incorporated to encouraged phosphorus accumulating organisms (PAOs) and requires anaerobic tank followed with aeration tank. Biological metal removal in turn happens by adsorption, complexation of metals with the negatively charged surface of microorganisms, transformations and precipitation. (Tchobanoglous *et al.*, 2003)

### **3.2 Challenges with biological and joint treatment**

Although activated sludge methods are common due to high cost-effectiveness on organic matter removal, they possess also some disadvantages. These include area requirement, high energy consumption due to aeration, temperature and condition dependency, addition of

nutrients, waste sludge disposal, dangerous and recalcitrant substances to microbes, slow recovery from setback and post-disinfection need (Tchobanoglous *et al.*, 2003). Moreover, some challenges can rise because of design or operational problems.

Major treatment problems occurring in wastewater treatment plants are related to fluctuations in temperature, pH and organic load and depletion of oxygen or nutrients. Rapid changes in temperature can hinder the activity of microorganisms and nutrient deficiency prevents the growth of biomass. Constant nitrogen supply is more critical than phosphorous, since P can accumulate into formed sludge. Excessive addition of nutrient can however lead to exceeding of discharge limits and cause eutrophication in receiving waters.

Severe fluctuations in influent loading effect the biological treatment in many stages. If BOD load increases and food to microorganisms ratio (F/M) is over 0.5, growth rate, sludge production and aeration need increase significantly. As a result, plenty of fresh flocs or filamentous bacteria are formed with non-flocculating and poor settling properties. On the other hand, with significantly low BOD load or F/M below 0.2 growth and BOD removal can be slow, but aeration requirement may increase due to endogenous respiration. (Davies, 2005)

Aeration efficiency of the aeration equipment can be exceeded with increased aeration need which results in decrease in oxygen level. Also, at higher temperature less oxygen dissolves into water. Oxygen depletion can cause breakdown of the biosludge and overgrowth of filamentous bacteria (Finnish Water Utilities Association, 2018). This kind of bulking sludge is problematic and can appear as foaming in the aeration basin. Too vigorous aeration can also break the good settling flocs. Sludge that settles poorly decreases clarification performance and quality of effluent. Additionally, increasing amount of resulting sludge and non-biodegradable and inorganic solids influence the properties of sludge like effectivity, settling, dewatering and utilization.

Challenges especially with industrial wastewaters are related to toxic, inhibitory and refractory compounds that can appear in a larger extent than would be desirable for biological treatment. Toxins hinder the metabolic reactions of bacteria which lead to interference with respiration and growth i.e. removal of organic pollutants and sludge

production (Davies, 2005). Inhibition can occur also as delaying growth retarding phenomenon, which is passed with time and accustoming (Laukkanen, 2008). Inhibiting concentrations of some toxins to activated sludge are presented in Table III.

**Table III** Inhibition concentrations of substances to activated sludge (Ullmann's, 2000)

Substance	Inhibiting concentration, mg/L
<b>Cadmium (Cd<sup>2+</sup>)</b>	2–5
<b>Chromate (CrO<sub>4</sub><sup>2-</sup>)</b>	3–10
<b>Copper (Cu<sup>2+</sup>)</b>	1–5
<b>Nickel (Ni<sup>2+</sup>)</b>	2–10
<b>Zinc (Zn<sup>2+</sup>)</b>	5–20
<b>Chlorine (Cl<sub>2</sub>)</b>	0.2–1
<b>Cyanide (CN<sup>-</sup>)</b>	0.3–2
<b>Mineral oils</b>	> 25
<b>Phenols</b>	200–1 000
<b>Hydrogen sulfide/Sulfide</b>	5–30

Aerobic treatment of recalcitrant compounds is difficult due to the reason that they have no transformation during biological treatment or generated degradation products are also inert or otherwise harmful. Although toxic and recalcitrant compounds are not biodegraded, nonbiological and abiotic losses occur. These compounds can be removed by adsorption onto the biomass (solids partitioning) and volatilization. (Tchobanoglous *et al.*, 2003) However, removal efficiency is affected by properties of substances and treatment conditions (Luo *et al.*, 2014). Nonbiodegradable compounds can accumulate into water sources especially into sediments if they are not eliminated. Also, the emerging organic contaminants can have detrimental effect on aquatic ecosystem and human health. (Galanakis&Agrafioti, 2019)

Knowledge about biodegradation of these recalcitrant compounds has been increasing, exposing the capabilities and limitation of biological treatment. Most of these compounds are able to eventually biodegrade but it is so slow that available treatment time, hydraulic retention time (HRT), is not long enough, or unique conditions or specific microorganism are needed. Microbes can also readjust to new compounds. Acclimation time of microbes to induce and sustain enzymes can take hours to weeks. Better way to accustom microbes is to add constant over intermittent supply of new compound. Exposure can be done in a

laboratory and then the actual plant could be seeded with the accustomed microbes. (Tchobanoglous *et al.*, 2003)

Centralized treatment plants, industrial parks and chemical sites wrestle in addition to resistance to biodegradation with challenges concerning variability of streams, water shortage and wide distribution of complex compounds (Bauer *et al.*, 2019). With joint treatment of wastewaters, it is difficult to trace the responsibility of different origins for the performance and quality of final discharged wastes. Flexibility of the wastewater management can be more restricted and total cost-benefits and efficiency lower than with smaller, targeted on-site treatment processes. (Brinkmann *et al.*, 2016)

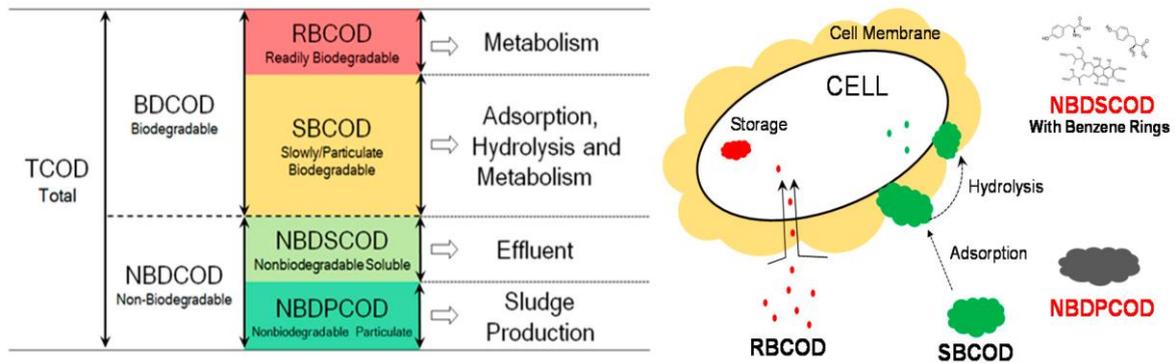
Mixed wastewater contains streams from different industrial sectors and origins. It is justified to require pre-treatment of complex streams before discharge to the centralized treatment plant to maintain the performance. On the other hand, knowledge on the biological decontamination ability of wastewater that has been processes several times and has ultra-low concentration is not available. (Lei *et al.*, 2010) Separate treatment and collection of wastewaters with different characteristics like high salt, poorly degradable or toxic concentrations is proposed in the treatment plant. Also, water reuse with fit for purpose concept inside the industrial park might arise. (Bauer *et al.*, 2019) In any case, vigilant control of process parameters in treatment plant dealing with a wide range of wastewaters is needed (Davies, 2005).

### **3.3 Importance of wastewater characterization and determination of biodegradability**

To tackle problems arising from design or operation, wastewater characterization indicating quantity and quality of the specific stream from biological, physical and chemical perspectives has an important role (Sperling, 2007). Information about amount and availability of organic components and nutrients N and P will tell if aeration and volume capacity is enough or nutrient supplements are needed. Alkalinity will tell how well favorable pH is maintained. Inhibition and foaming potential are also important features to be tested. When new streams are introduced to the plant, it must be known that the capacity is enough, major operation problems should not occur and the terms of the permits are fulfilled.

Since the actual chemical composition of effluent can be diverse and not fully identified, use of indirect or sum parameter like TOC and COD gives better estimation of the polluting potential (Hynninen, 2008). The fundamental difference between these parameters is that TOC value tells amount of organic carbon measured as resultant CO<sub>2</sub> from combustion and COD amount of oxygen measured as used dichromate in the oxidation process (Davies, 2005). Carbon content in the influent wastewater have vital impact the biological treatability and thus design of the treatment systems, especially for complex industrial wastewaters (Baban, 2013). Considering the biological treatability, total TOC and COD results might give misleading information, since values include stable and recalcitrant organic carbon compounds and possibly oxidizable inorganics, resulting overestimation of removable carbon.

Therefore, assessment requires understanding of COD fractions. (Cokgor, 1997; Baban, 2013) COD is divided into biodegradable and non-biodegradable fractions with their soluble and particulate subdivisions. The common fractionation of COD and their fate in treatment plant is presented in Figure 3. More detailed fractionations consider also volatile, adsorbable and biomass fractions. COD fractions are used for modelling of treatment plants. Although COD fractions are considered so important, no uniform methodology for determination of COD fractions or classification on colloidal fraction exists. (Myszograj *et al.*, 2017) Besides, no standardization on the definition between soluble and particulate fraction exists, since it is depending on the pore size of the filter or precipitation (Tchobanoglous *et al.*, 2003). Degradation, removal mechanisms and resource recovery potential can be evaluated also with molecular and particulate size distribution. Ultrafiltration (UF) or size exclusion chromatography are used to characterize the compounds of the effluent based on molecular weight. UF is commonly used for pulp mill effluent characterization. (Yousefian, 2000)



**Figure 3** COD fractions (Choi *et al.*, 2017).

Inert fractions are usually determined by calculating the difference between total COD and biodegradable part. Inert COD goes through biological treatment without change. Soluble part ends up without reactions into the effluent and eventually into receiving waters. Particulate inert fraction accumulates into biomass. It is partly removed from the process with excess sludge and partly returned by recycled sludge to the aeration basin. These non-biodegradable particulates increase the mixed liquor suspended solids (MLSS) concentration and reduce its biologically active fraction (Baban, 2013) Due to the inert COD, stringent COD reduction regulations cannot be met solely with conventional biological treatment by adjusting process parameters. (Cokgor, 1997)

Biodegradable fraction of COD is generally determined by respirometry. Estimated value can also be derived by chemical-physical analysis, in which sample is flocculated with zinc sulfate and filtrated. The biological measurement is based on the uptake of oxygen by microorganisms through their respiratory activity in catabolism reactions to yield energy from carbon compounds. Measurement does not consider the carbon that is not oxidized and ends up on growth of new biomass through anabolisms (Davies, 2005). Heterotrophic yield coefficient can be used to count that part. Even 20-50% of carbon is converted into new cells depending on the usability and energy yield. (Saski, 1998)

Biodegradability is important water quality criteria because it tells the biological response of microorganism to their food i.e. organic pollutants. Wastewater entering biological treatment should have high BOD to COD ratio, usually over 0.5 is considered easily treatable and below 0.3 non-biodegradable. Disadvantages of BOD measurement are that it cannot be

used to describe pollutant load of wastewater and material balance of waste water treatment (Baird&Smith, 2002). Measurement is time-consuming, which does not make it a good operating parameter and results may vary due to variability in the microbial population in used inoculum. (Jouanneau *et al.*, 2014).

Common factors in biological measurements are determination of dissolved oxygen or oxygen consumption, seeding with optional inoculum, dilution and addition of nutrients and nitrification inhibitor if needed and incubation at constant temperature (normally 20°C) in dark for a certain period of time. Methods for measuring the dissolved oxygen or oxygen uptake are iodometric, electrochemical and optical probes and photometric and manometric methods (Jouanneau *et al.*, 2014). Inoculum can be effluent from treatment plant, sludge from aeration basin or population from e.g. surface water. Incubation time is five or seven days depending on the BOD measurement standard and in longer biodegradability tests 28 or even 60-90 days.

The result from a standard BOD measurement is single value of consumed oxygen. More information about the biodegradation reaction is received from the continuous readout of respirometers. Changes in the shape of oxygen uptake curves can indicate lag, toxicity and unusual pollutants. The toxic or inhibition effect of treated wastewater should be considered, both for the sake of activated sludge in the treatment plant but also its impact on biodegradation test results. In the determination of readily biodegradability, the consumed oxygen is compared to theoretical oxygen demand or COD. Sample is considered readily biodegradable if 60% is degraded in 10-day window. (APHA, 2004) There is also different rule of thumbs and equations to convert BOD results to ultimate biodegradation and biodegradable COD values.

One of the commercial respirometric device is OxiTop® (WTW). Oxygen measurement is manometric i.e. based on pressure measurement. Advantages of OxiTop method are good measurement repeatability, easy maintenance, automatized measurement, faster preparation of measurement compared to conventional BOD measurement and wide measuring range convenient to use for highly polluted samples. It is a practical tool for studying different phenomena. (Björklund, 2015, Laukkanen, 2008; WTW, 2000) Oxitop has been used previously in studies to measure the biodegradability of substance or biodegradable part of

COD or toxicity (Ravndal *et al.*, 2018; Roppola, 2009; Myszograj *et al.*, 2017; Płuciennik-Koropczuk *et al.*, 2017; Vankova, 2010; Vähäoja, 2004; Laukkanen, 2008). In addition to more traditional BOD measurement methods, quicker and less deviation causing methods has been developed. These includes different kind of biosensors with bioluminescent or entrapped bacteria, redox mediator, microbial fuel cells and bioreactor. Many of these methods however need a statistical correlation model for predicting the corresponding BOD value. (Jouanneau *et al.*, 2014) Respirometer simulates actual microbe population and conditions at wastewater treatment plant in a smaller scale (WTW, 2000).

#### **4 FEATURES OF BIOCHEMICAL WASTEWATERS**

The pulp and paper industry is known for its large consumption of water and effluents containing recalcitrant and toxic compounds (Pajpai, 2018). However, significant development has achieved in the treatment of process waters and wastewaters enabling reductions in pollutant and volume loads to treatment plants (Hubbe *et al.*, 2016) Compared to conventional forest industry, similar wastewaters related to the biorefinery are generated from the preliminary wood handling including debarking, chipping and chip washing and handling. Although the wood handling process and its wastewaters are generally well-known, the raw material of new biorefinery is not traditional.

The main raw material used is European beech (*Fagus Sylvatica L*). Oversupply of sustainable sourced beech wood in Germany supports the industrial use of such wood to add its converting value (UPM, 2020). Other hardwood may be used as well. The basic constituents in hardwood are 40-45% cellulose, 30-35% hemicellulose and 20-25% lignin. Compared to softwoods, there is less lignin and more hemicellulose. These are the cell wall structure components with high molecular weight. Distribution of main constituent in beech wood and its smooth silver-gray bark are presented in Table IV. The exact content depends on the moisture content, habitat, age, plus growing and preservation conditions of the wood. (Alén, 2000)

**Table IV** Constituents in beech wood and bark.

<b>Beech</b>	<b>Cellulose</b>	<b>Hemicellulose</b>	<b>Lignin</b>	<b>Extractives</b>	<b>Others</b>	<b>Reference</b>
<b>Wood</b>	39.4	33.3	24.8	1.2	1.3	(Sjöström, 1993)
<b>Bark</b>	38.1	23.1	39.1	11.4	7.3	(Dietrichs <i>et al.</i> , 1978)

New type of wastewaters originates from the biochemical processes in which wood is converted into sugars and further into end products. Streams include also cleaning and washing waters of unit processes. Recycling of process waters have been designed in a way that generated discharges are minimized. Recovery of valuable components from these wastewater streams is commercially very challenging. Elements of wood, auxiliary and process substances and chemicals can be present in their original or changed form (Finnish Water Utilities Association, 2018). The distribution of components is wide. Some of the substances are easily biodegraded by microorganisms but there are also toxic, mutagenic or slowly degradable compounds which can accumulate to streams and living organisms. These can pose risks to process and treatment performance, aquatic ecosystem and human health. (Yousefian, 2000)

#### **4.1 Wastewaters from wood handling area**

Waterless wood handling is not favorable, since the dirt should be removed from the raw material before further processing due to high clean quality requirement. Wood handling discharges contain impurities like rocks, sand and soil, wood derived solids like bark and fibers and variety of colloidal and dissolved organic substances together with nutrients and minerals. Dissolving of compounds depends on the type of biomass and concentration of used water. Debarking is essential part in primary wood handling, if bark is resistant to further treatment and causes process and product quality problems. (METLAS KY, 1989) The bark is a protection mechanism of wood against microbial attacks which is associated to the presence of phenolic compounds and their antibacterial property (Petraakis *et al.*, 2011).

It is suggested that the secondary chemistry of beech i.e. engagement of phenolics in the biosynthesis of lignin is responsible for low insect species diversity in beech trees (Petraakis *et al.*, 2011). In addition to the hydrophilic extractives, water extract of bark is supposed to be consisting of, carbohydrates, acids, alcohols and other small molecular compounds. Wood

bark is also a significant source of nutrients and minerals, especially phosphorus. (Saunamäki, 1994; Finnish Water Utilities Association, 2018) Beech bark water extract was identified with compounds like vanillic acid, gallic acid, quercetin, taxifolin, syringic acid, coumaric acid, syringin, protocatechuic acid, chlorogenic acid, ferulic acid and isoquercitrin. Data about the biological activity of these extractives is limited, but some were observed to have low antimutagen effect and strong free-radical-scavenging indicating antioxidant ability. (Tanase *et al.*, 2019)

Most of the pollutants in wood handling waters are removed mechanically and biologically. Debarking plants usually have their own clarifiers to separate bark, other solids and fine particles from wastewater. Sometimes bark needs pressing and pressate can cause 80-90% of BOD and COD load of whole debarking discharges (Saunamäki, 1994). Bark with a suitable dry matter is burned for energy, but the use of bark as a source of bioactive compounds for different commercial and biomedical applications is under research. (METLAS KY, 1989; Tanase *et al.*, 2019) Challenges with debarking waters arise from their toxicity and acidity.

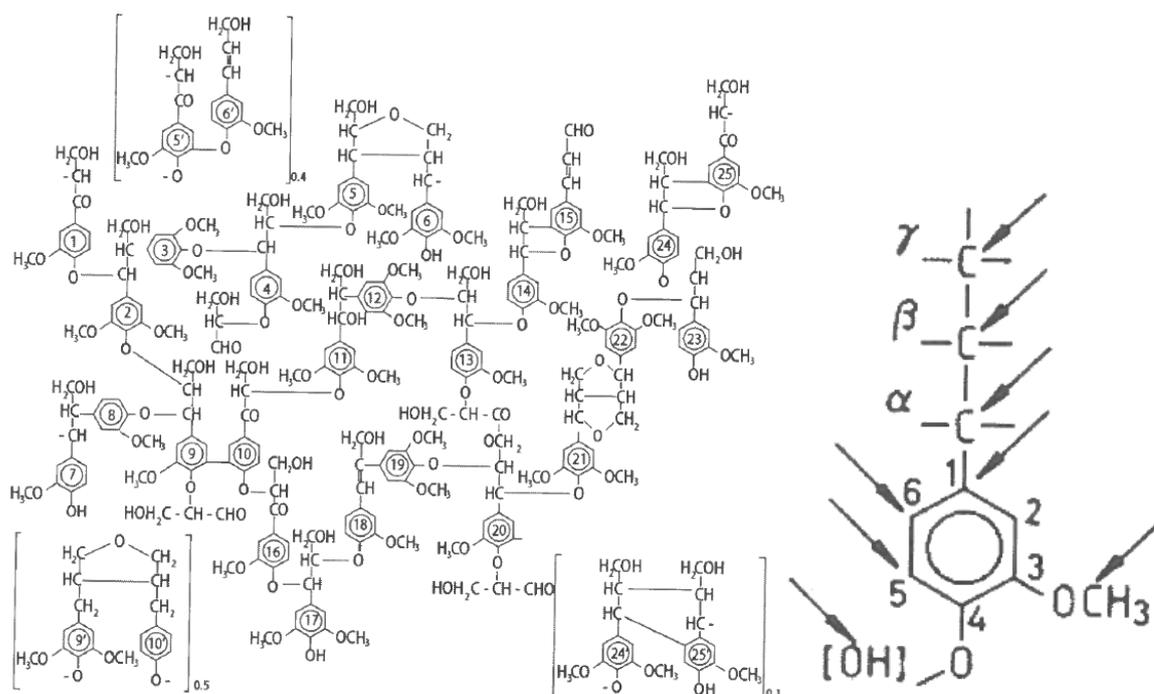
Debarking water can be significantly toxic to fish even below LC50 values of 5% due to high concentration of extractives (Saunamäki, 1994). When different softwoods and hardwoods were compared, beech bark was considered as the least toxic wood studied (Field, 1989). Softwood toxicity is due to high resin acid content, which are not present in hardwoods (Routa *et al.*, 2017). Also, the pH of beech bark water extraction is less acidic, between 5.0-5.5, when the pH from softwood and oak can be below 4 (Kettunen, 2006). In spite of these characteristics, pre-clarified wood handling waters can be jointly treated biologically if the dilution effect in the treatment plant is sufficient. Otherwise pre-treatment to eliminate toxicity or other methods should be considered. (Saunamäki, 1994)

## **4.2 Features of main organic components**

The dissolved and residual carbohydrates and carboxylic acids like monomer sugars, acetic acid and other low molecular weight organic acids in the wastewater streams are mostly quick and easy food for microorganisms in the treatment plant. They are derived from wood polysaccharides. Cellulose consists of glucose with polymerization degree of 8 000-10 000

(Kettunen, 2006). Primary hemicelluloses in hardwood are glucuronoxylan, which has acetyl groups, and glucomannan (Alén, 2000). The main non-glucosic building units of hemicelluloses in beech are mannose (0.9%), xylose (19.9 %), galactose (1.4%), arabinose (0.7%), uronic acid (as 4-O-methylglucuronic acid 4.8%) and rhamnose (0.5%) (Fengel&Wegener, 1989). Structurally glucosidic linkages, hydroxyl groups of sugar units and end-groups of polymers are prone sites to degradation reactions and attacks. Under certain degradation conditions (different pH, temperature and reactants) aromatic, condensed and volatile degradation compounds like furfural can also form (Kettunen, 2006).

Lignin in the wastewater streams can be as colloidal suspension or in dissociated and soluble form. It is considered as one of the most recalcitrant wood-based compound, especially to biological treatment, inhibiting waste management and whole biodegradability of lignocellulosic streams (Kindsigo, 2009). The chemical structure of lignin is originally irregular and complex, consisting of phenylpropane unit polymers with hydroxyl and methoxyl groups. Hardwood lignin, referred as guaiacyl-syringyl lignin, is composed of trans-coniferyl alcohol and trans-sinapyl alcohols. (Alén, 2000) Model structure of beech lignin with 25 building units and their major reactions sites are presented in Figure 4.



**Figure 4** Model structure of lignin from beech and principal reaction sites of phenyl propane unit. (Kettunen, 2006)

Because of the random polymerization, indefinite structure, various functional groups and linkages like ethers, carbon-carbon bonds and esters between building units and lignin-carbohydrate complexes, understanding lignin degradation reactions is challenging (Alén, 2000; Kettunen 2006). Different chemical, physical and biological treatments change the structure and properties of lignin. Basically, lignin reactions occur at the propane side-chain, aromatic ring or at the functional groups of which the phenolic hydroxyl group is less frequent than the methoxyl group (Kettunen, 2006).

Wood extractives are a group of low molecular weight organic components mostly derived from glucose. The composition of extractives is not single determined because the solubility depends on the type of solvent. Wide range of hardwood extractives include water-soluble phenolic compounds like flavonoids, lignans, stilbenes and tannins and lipophilic fats and waxes like fatty acids, sterols, steryl esters and triglycerides. (Isotalo, 2004; Alén, 2000; Routa, 2017; Holmbom, 2011) Most of the wood extractives can be removed by activated sludge processes via degradation and adsorption (Kostamo&Kukkonen, 2003). Lipophilic extractives that adsorb onto biosludge, are resistant to biodegradation and can cause environmental concern (Yousefian, 2000). The remain extractives and their metabolites end up into receiving water and eventually into sediments. From the contaminated sediments they can dissolve to water due to oxygen deficiency, erosion or dredging of sediments (Meriläinen *et al.*, 2006).

These above-mentioned organic compounds are the main source for COD in the biorefinery effluents. Conversion factors for different organic substances and groups from mg/L concentration to COD concentration  $\text{mgO}_2/\text{L}$  are presented in Table V. The table also includes information about their contribution to BOD. In addition, some streams can contain residuals of the main product monoethylene glycol (MEG). It is tested to be readily biodegradable aerobically and anaerobically with different microbe populations. Pure MEG has low toxicity to aquatic organisms and capacity for bioaccumulation. It should not be confused with commercial deicing products containing MEG that have higher toxicity due to other components. (Dobson, 2000)

**Table V** Contribution of the most frequent organic compounds in biorefinery effluents to biological and chemical oxygen demand. (Yousefian, 2000)

Compounds	Contribution to BOD	Conversion factor for COD
Carbohydrates	Readily biodegradable	1.2
Acetic acid	Readily biodegradable	1.1
Formic acid	Readily biodegradable	0.35
Lignin	Recalcitrant	1.9
Extractives	Degradable or toxic	2.7
Methanol	Readily biodegradable	1.5

### 4.3 Features of main inorganic components

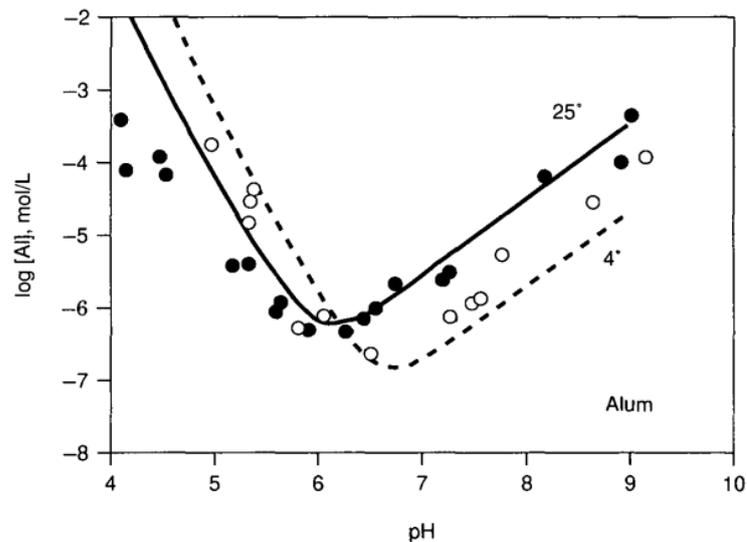
Inorganic components originate both from wood and process chemicals and from fresh water (Leiviskä, *et al.*, 2009). In wood they are present in minor quantities. In bark and other living parts of tree they are more abundant than in stemwood. Configuration varies between the growth environment since salts and nutrients are taken up to the tree by roots from soil. (Alén, 2000) Nitrogen is mainly bound to wood constituents and proteins. Heavy metals and other trace elements from production processes end up practically completely in the wastewater streams. Depending on the concentration and speciation of these elements, their toxicity, bioavailability and tendency to cause corrosion varies. (Skipperud *et al.*, 1998) Main cation and anion ending up in elevated concentrations to some wastewater streams are sodium and sulfate. High salinity can cause osmotic stress to microbes leading to dehydration and lysis of cells and reduction of microbial growth and population (Yan *et al.*, 2015).

Waste alkali stream contains water soluble aluminum salt. Solution is strongly alkaline, because aluminum accepts protons and releases hydroxide ions from water. The dissolution reaction is described in equation (2):



Under acidic conditions, aluminum occurs predominantly as  $\text{Al}^{3+}$ , but forms  $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_2^+$  occur too. Under neutral to alkalic conditions dominant form is  $\text{Al}(\text{OH})_4^-$ . Often the solubility of aluminum is however exceeded which results in hydrolysis reactions and generation of amorphous and gelatinous aluminum hydroxide  $\text{Al}(\text{OH})_3$  precipitate.

Aluminum solubility is influenced by concentration, pH, temperature and presence of complexing agents like organic matter, chloride, sulfate and phosphate. (McEwen, 1998) Solubility of aluminum as a function of pH in two different temperatures is presented in Figure 5. In aquatic environment, aluminum is mainly toxic to fish and plants at pH values below 5.5.



**Figure 5** Theoretical solubility (solid and dashed lines) of aluminum in equilibrium with  $Al(OH)_3$  and experimental data (black and white dots) of dissolved alum at 25°C and 4°C. (McEwen, 1998)

#### 4.4 Color

Wood contaminated waters can have characteristic color from light-brown to dark. Color can be due to lignin, humic matter, extractives or metals such as iron. (Hubbe *et al.*, 2016) It can be used as an indicator to inhibitory compounds present in water (Springer, 1993). Dark color is proposed to originate for example from oxidation products of tannins (Saunamäki, 1994). Linear dependency between lignin and color was observed by Kindsigo (2009). Color is not removed by biological treatment, and it can even darken after the treatment, which may be due to the release of initially adsorbed color causing substances back to the wastewater on settling (Slade, 2010). Color removal is not typically required in wastewater permitting, but color causes aesthetic harm (Finnish Water Utilities Association, 2018).

#### 4.5 Residuals from anaerobic pre-treatment

Condensates and other suitable streams having easily degradable and non-toxic character to methanogenic degradation are directed first to anaerobic treatment. Anaerobic treatment occurs without oxygen, where anaerobic organisms convert organic matter into methane enabling energy recovery as biogas. This way high-strength organic streams can be treated with lower biomass yield and savings in energy and nutrient consumption and reactor volume. (Tchobanoglous *et al.*, 2003)

Some biorefinery streams bypass the anaerobic reactors due to inhibition potentiality of high lignin, extractives or sulfur content. Recalcitrance of lignocellulosic substrates might limit the microbe growth and lead to less diverse microorganism population. (Nguyen *et al.*, 2019) Toxicity of wood handling streams like debarking effluents are associated with extractives and especially softwoods' resin acids. High sulfate concentration cause growth of sulfate reducing bacteria, which compete with methanogenic organisms and generate toxic sulfide to them. The ratio of COD and sulfur should be kept above 30 to prevent decrease in performance. (Pichon *et al.*, 1988) Detoxification and elimination of inhibition can be achieved by co-digestion, dilution with other wastewater streams or pre-treatments such as precipitation and solids removal.

Typical features of anaerobic effluent are devoid of DO, rich in nutrients like ammonia and phosphate, reduced species and runaway granule. COD concentration from well-functioning treatment is from 50 to 200 mg/L. (Khan *et al.*, 2013) Effluent quality does not usually meet requirements for direct disposal and therefore anaerobic treatment is followed by aerobic post-treatment. (Tchobanoglous *et al.*, 2003) Aeration achieves oxidation of odour causing sulfides back to sulfate and reduces residual organic and nutrient load. Khan *et al.* (2013) discovered that suspended growth is suitable for treatment of anaerobic effluent. They proposed that SBR is better option than ASP because of compactness, flexibility and efficient nutrient and COD removal. Activated sludge processes for concentrated sewage and anaerobic effluents were seen less sustainable option due to the linearly increase of aeration cost with organic load. (Khan *et al.*, 2013)

## 5 PRE-TREATMENT OPTIONS FOR RECALCITRANT COD

Application of wastewater treatment methods depends on, besides composition and type of wastewater, the concept of wastewater treatment in particular biorefinery and existing facilities. Wastewater that is being circulated back to process or discharged to receiving water at site or further to centralized treatment plant have different requirements and assets and choice of suitable treatment method can vary according to that. Nonetheless, better integration and optimization of wastewater treatment technologies with bioconversion process gain overall resource efficiency and reductions in need and cost of wastewater management (Tobin, 2020).

Before biological treatment, purpose of the utilized physical or chemical pre-treatment methods is to remove or degrade non-biodegradable COD and toxicity to enhance biodegradability. The BREF document for chemical industry recommends pre-treatment by chemical or wet oxidation to remove refractory organic pollutants from streams that are destined to biological treatment (Brinkmann *et al.*, 2016). On the other hand, efficient technologies like adsorption, advanced oxidation processes (AOPs) and membrane technology have been developed and applied for challenging industrial park wastewaters (Lei *et al.*, 2010). In addition to these methods different hybrid and commercial systems are also available and novel and emerging methods are under development.

A wide range of different methods can cause problems in selection and in the adaption of design and operation, if process kinetics are not properly understood (Lei *et al.*, 2010). Treatment efficiency can be enhanced with optimization, but the choice is influenced by economical, operational and environmental aspects and suitability to specific case like applicability on an industrial scale and for diluted or concentrated stream. Some of the techniques are too expensive to be economically viable. High cost restricts their application and demand for cost-effective and efficient techniques is real. (Lei *et al.*, 2010) Sometimes reductions in costs due to lower energy and chemical consumptions, treatment time and contaminant load to following treatment can be achieved by treating highly concentrated streams separately rather than if they were mixed with other streams.

## 5.1 Methods based on separation technology

In separation technologies, pollutants are transferred into another phase or concentrated into waste stream. Treatment should be targeted to the inert COD fraction in order to improve biodegradability. Advantages of these methods as a pre-treatment are that they are easily scalable and can be selective. Disadvantages are that further treatment and disposal of concentrate, used separation material or regeneration stream is needed. Recovery of valuable compounds though could be possible. Such methods include for example adsorption, coagulation/flocculation combined with solids removal, precipitation and membrane technology with their electrochemical configurations.

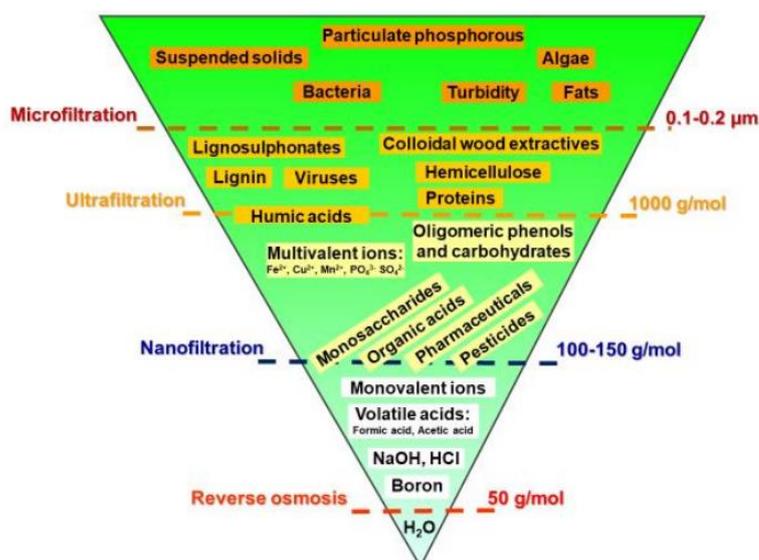
Precipitation is elimination of soluble contaminants by adding precipitant agent or changing solution conditions such as pH. Solubility of substance is unbalanced and solid precipitate forms. Precipitation should be applied close to origin, before dilution effect impair efficiency. Method is applied principally to heavy metals and other inorganics, but also for some organic compounds. At least stirred mixing tanks, solid separation and precipitant sourcing and storage are needed. (Brinkmann *et al.*, 2016) Reductions in inert COD, microbial products and increased biodegradability has been achieved with chemical precipitation as a pre-treatment before biological process (Baban, 2013). For example for lignin, acid precipitation by sulfuric acid, chlorine or carbon dioxide is used (Humpert *et al.*, 2016).

Coagulation/flocculation methods enhance solid-liquid separation by destabilizing solids. Actual separation can be performed for example with flotation. Efficiency is dependent on solution conditions, agent and its dosing and mixing speed and time. (Sillanpää, 2015) Typical coagulants are aluminum and iron salts. They are suitable for broad range of water pollutants, mostly for colloidal particles but also for some dissolved organic compounds. The mechanisms are based on charge neutralization of negative charged colloids by cationic hydrolysis products and so-called sweep flocculation in which pollutants are incorporated in an amorphous hydroxide precipitate. (Duan & Gregory, 2003) There are also efficient composite coagulants for lignin removal. Yaser *et al.* (2014) reported that use of calcium for lignin containing waters from pulp, paper and olive oil mills produced more biodegradable treated water than conventional aluminum and iron salts. For lipophilic extractives high

removal rates from debarking effluent has been achieved with chitosan and kaolin coagulants using doses of 30-85 mg/L and 2-5g/L, respectively (Leiviskä *et al.*, 2012).

Treatment can be applied for separate concentrated fractions (Hynninen, 2008). Disadvantages of using coagulation/flocculation chemicals are addition of superfluous anion with the agent and formation of waste sludge with the functional cation. When electrochemistry is utilized in coagulation or flotation by electrolytic cell, reductions in chemical consumption and sludge generation are achieved and formed flocs are more compact. Efficiency enhances and is affected by electrode material, pH, T, current density, and conductivity. However, electrochemical methods consume lots of energy and electrode materials must be renewed after wearing. (Sillanpää, 2015) With complex wastewater composition, prediction of reactions and results is uncertain and difficult without testing. (Brinkmann *et al.*, 2016)

Membrane technologies are energy intensive filtration processes through semi-permeable membrane. The driving force can be for example pressure difference. According to the cut-off value, membranes can be divided into micro- (MF), ultra- (UF), nanofiltration (NF) and osmosis processes (RO, FO). They are described as the most effective for recalcitrant compounds removal from wastewater because complete removal of contaminants is possible. (Hubbe *et al.*, 2016) Permeate is filtrated through membrane and rejected contaminants are concentrated into the retentate stream. Figure 6 illustrates applications of different pressure driven membrane processes. Treatment efficiency is dependent on membrane material and format, cut-off, pressure, feed flow, pH and hydrophobicity/-philicity. Downsides of the method can be membrane fouling and short membrane service time. Combination of membranes and electrochemistry is electrodialysis, in which the driving force is electrical potential. This is applied mostly for ion removal, but removal of charged organic compounds is also possible.



**Figure 6** Removal of contaminants by pressure-driven membrane processes based on molecular weight cut-off values. (Mänttari, 2018)

Adsorption is a method, where wastewater is treated with a porous material. Pollutants are adsorbed into the media due to high surface area and affinity. Method is easy to implement as mixing or packed columns processes and has rather low operating cost, since no high pressures are needed. Operation requires replacement or regeneration of adsorbent and preceding removal of solids. Macromolecules can reduce adsorption capacity by irreversible blocking and also versatile component content can decrease efficiency. Treatment efficiency is dependent on pH, temperature and of course adsorbent material. They can be inorganic minerals or organics, of which activated carbon is found to be efficient for toxic, colored and aromatic compounds and most commonly used. (Sillanpää, 2015; Sillanpää & Shestakova, 2017, Hubbe *et al.*, 2016) High performance adsorbents can be very expensive, so the production of cost-effective of materials is a compelling subject of research. Application of nanotechnology and waste raw materials have been studied (Bui *et al.*, 2019). Different biosorbents like sludge derived adsorbents are seen as cost-effective solutions.

## 5.2 Methods based on oxidation processes

In the oxidation of persistent organic compounds, a structural change or conversion to readily biodegradable organics or total mineralization to H<sub>2</sub>O and inorganic CO<sub>2</sub> is achieved. Processes are good pre-treatment options, since partial oxidation contributes the treatability

further in subsequent biological treatment. However, oxidation is not selective, so easily oxidizable BOD degrades too. Structural change can lead to elimination of toxicity or more toxic degradation products and recalcitrant by-products. These methods are mostly applied for soluble contaminants and streams containing solid particles need pre-treatment step before application. (Sillanpää, 2015; Hubbe *et al.*, 2016, Brinkmann *et al.*, 2016) Oxidation processes include conventional methods like ozonation, variety of advanced oxidation processes and their electrochemical configurations.

Ozonation is widely used in wastewater treatment. Oxidation is achieved directly via ozone attack and indirectly by hydroxyl radical formation in specific pH range of 4-9. Ozone is selective towards double bonds, amines and aromatic groups due to its dipole structure. Generation of ozone from oxygen by electrical discharge is required on site, which makes it energy intensive process and yields are typically low. Biodegradability of complex industrial park wastewater has been improved by ozonation. (Fanchiang *et al.*, 2009) As a drawback generation of ozonation by-products is possible. These compounds can be recalcitrant to further degradation in low concentrations, smaller molecular weight compounds being more recalcitrant than bigger compounds. Ozonation can be coupled for example with catalyst, peroxides, UV or ultrasound to enhance efficiency. (Brinkmann *et al.*, 2016, Sillanpää, 2015)

AOPs are variety of oxidation processes that generate and use hydroxyl radical, a strong active oxidant, and other reactive oxygen and chlorine species for oxidation of recalcitrant compounds. Only fluorine and  $\text{TiO}_2$  have higher oxidizing power than  $\text{OH}^\bullet$  and methods work for compounds recalcitrant to oxygen, ozone and chlorine. (Kindsigo, 2009) AOPs include technologies such as non-photochemical, photochemical (restricted for high turbidity waters), non-thermal, electrochemical and catalytic processes (hetero or homogeneous noble metals, transition metals oxides or salts complexes), hot AOPs, ultrasound, cavitation, electron beam irradiation, and their variations and combinations.

Wet oxidation (WO) processes are suggested for efficient pre-treatment for recalcitrant and harmful contaminants in moderately or concentrated concentrations. Oxidant source in WO can be either air or hydrogen peroxide and processes are operated in elevated temperature and pressure often with a catalyst. Technology cost is relatively low, but operation costs are

high. (Brinkmann *et al.*, 2016) Good results as partial oxidation to improve biodegradability and remove lignin from model water solutions has been achieved (Kindsigo, 2009).

Fenton is an efficient example of catalytic AOP. The process involves hydroxyl radical generation by adding  $H_2O_2$  and ferrous ions. Advantages of  $H_2O_2$  use are that it is an inexpensive and abundant chemical. Disadvantages of Fenton reagent include formation of iron sludge and variability in process efficiency with different waters. Dissolved organic matter can have useful impact to Fenton process, because they can form complexes with ferric ions. Fenton can be coupled with UV and electrochemical processes which may solve some technical or economic challenges. Technique is still less utilized at industrial scale than ozonation. (Hubbe *et al.*, 2016)

Gas phase pulsed corona discharge (PCD) is a good example of non-thermal plasma process that has been noted as a potential wastewater treatment method and reached the commercial stage. PCD could be more cost efficient and safer option for conventional ozonation. Main oxidizers in PCD, ozone and hydroxyl radicals are generated inside the reactor by electrical pulse discharges from high voltage pulse generator. Therefore, treatment does not need any chemical additions. Compared to other plasma oxidation technologies, PCD has an advantage of higher plasma-liquid contact surface area. (Ajo, 2018) In addition, it is applicable despite the color of water, which is a major asset for treating lignin containing waters. Previous studies with wood-derived wastewaters have been promising, but suitability of PCD unit so far has been restricted due to large flows.

## **EXPERIMENTAL PART**

### **6 MATERIALS AND METHODS**

Experimental part was performed to the extent that representative samples were available. Some earlier studies are discussed with and as a complement to the new results. Even the representativeness was sometimes difficult to estimate, because the biorefinery does not yet exist and processes are still seeking for their true format. Moreover, used wastewater samples were not fresh due to the trial schedules, arrival of measurement systems and distance between sampling and laboratory.

## 6.1 Samples and wastewater stream flows

Samples representing actual wastewater streams were obtained from different pilot or laboratory trials. Original samples were kept frozen at  $-18^{\circ}\text{C}$  until sampling for this thesis. Samples used in this thesis were frozen again until handling and analyzes if needed. Exception was waste alkali stream, which was stored at cold room at  $4^{\circ}\text{C}$ . Ash containing stream was derived from trials on January 2020 and April 2020. The former, older sample was used as a basis for composition characterization and biodegradation tests. The latter was collected only for PCD pre-treatment tests. Anaerobic effluent sample was from a trial on February 2020, wood handling stream from a trial on September 2019 and waste alkali stream from a trial on July 2019. 5 liters of ash containing and wood handling streams were sent frozen from UPM Research Center (NERC) to external lab to Toihan Oy on 12.2.2020. Samples were received at the other end also frozen. Consistently the inoculation material from Leuna ZAB was collected on 18.3.2020, frozen and shipped to NERC following day.

Ash containing stream has opaque dark brown color, no major suspended solids and is alkaline with pH of 9.5. TOC value was 2250 mg/L, indicating high organic load. From total ICP result of 7340 mg/L, dominant inorganics determined were sodium (65%) and sulfur (35% mainly as sulfate-sulfur). Wood handling stream had lighter yellowish-brown color, suspended solids were present as tiny wood originated pieces. The stream had acidic pH of 4 and its TOC content was 1460 mg/L. Most abundant inorganics were trace minerals from wood like calcium, potassium, sulfur and magnesium. Anaerobic effluent had dark anaerobic granule as suspended solids, low organic load as TOC (40 mg/L), residual minerals and chloride derived from added mineral medium for the operation of the pilot and pH of 8.6. Waste alkali stream contained aluminum in liquid and solid phase with high pH of 12.8. Complete characterization results are reported in Appendix I Tables I and II.

The connection between samples and actual wastewater composition is based on evaluations of main streams planned to enter aerobic treatment. Mixing requirements, discharge limits and risks to ZAB and pre-treatment need are speculated according to the flows and COD loads that are presented in Table VI. Heavy metal concentrations under mixing requirements in biochemical process effluents were evaluated according to the flow data and ICP results.

**Table VI** Estimated flow and COD load of main biorefinery streams to aerobic treatment.

Stream		Flow, m <sup>3</sup> /h	COD, t/d
<b>Anaerobic effluent</b>		158	5
<b>Biochemical process effluents</b>	Ash containing stream	24	2.76
	Wood handling stream	16	1.92
	Waste alkali stream	6	-
	Other	41	-
	Total	87	4.68
<b>Debarking effluent</b>		32	0.44
<b>Total</b>		277	10.12

## 6.2 Chemical analyses

Chemical analyses for characterization and interpretation of test results were conducted at UPM NERC laboratories. Determinations were performed according to the methods shown in Table VII. From obtained concentration for each organic group, the corresponding COD concentration was calculated according to the conversion factors presented in Table V for COD. This is how the values for COD composition in soluble and colloidal fraction for ash containing and wood handling streams were obtained.

**Table VII** Methods used for wastewater sample characterization and composition analysis.

Determination	Instrument	Method
<b>pH</b>	Mettler Toledo CH-8603	Internal
<b>Suspended solids</b>		Internal
<b>COD<sub>Cr</sub></b>	Nanocolor 500D	ISO-15705
<b>TOC</b>	Shimadzu TOC-L	SFS-EN 1484
<b>Carbohydrates</b>	HPLC-RI 2	Internal
<b>Carboxylic acids, furans</b>	HPLC-PDA	Internal
<b>Soluble lignin</b>	Hitachi U-2900 Spectrophotometer	Internal, UV 205
<b>Extractives</b>	GC-FID	Internal, MTBE
<b>Total nitrogen</b>	Shimadzu TOC-L	SFS-EN 12260
<b>Metals, phosphorus</b>	ICP-OES	SFS-EN ISO 11885
<b>Anions</b>	IC	SFS-EN ISO-10304

### 6.3 Study of aerobic biodegradability and treatability

The requirement before mixing with other wastewater is considered to be met when 80% of soluble COD is determined as biodegradable. COD characterization for ash containing and wood handling streams were performed by Toihan Oy. COD (Hach LCK 514) and BOD (OxiTop®) was measured from raw sample and micro- and ultrafiltered (LMW) fractions of the streams. Microfilter was GFA with pore size of 1.6 µm and cut-off value of ultrafiltration membrane was 2 kDa. HMW fraction was calculated as a difference between microfiltered and ultrafiltered values. BOD was measured using respirometric measurement setup. Inoculum from paper mill ASP, nutrients N&P, nitrification inhibitor ATU and dilution water were added to pH adjusted and tempered wastewater samples. NaOH or HCl was used to adjust pH between 6.8 and 7.0. Incubation lasted for 24 days at 20°C.

In addition, toxicity or inhibition of samples to ZAB sludge were studied using OxiTop® 510 mL sample bottles and IDS measuring heads at UPM NERC. Measurement equipment is shown in Figure 7. Multi 3630 IDS digital meter was used for wireless operation of the measuring heads. First measurements with the new equipment were carried out for studying dilution and waste alkali stream addition effect on biodegradability of a mixture sample and measuring BOD<sub>5</sub> for anaerobic effluent. The mixture sample contained 15% by volume of wood handling stream, 30% of ash containing stream and 55% of dilution water. Dilution series measurement set included blank determination (0%) and sample at 5%, 10%, 20%, 40% and 80% of total volume. Waste alkali stream study included reference determination (mixture sample) and addition of alkali stream as 2% of total volume with and without pH adjustment. BOD<sub>5</sub> determination included blank determination and two replicates.

Samples were tempered to measuring temperature and pH was adjusted between 6.5-7.5 with 1N NaOH or H<sub>2</sub>SO<sub>4</sub>. Total sample volume in sample bottles were 100 mL for toxicity measurements and 300 mL for BOD<sub>5</sub>. Sample volume contained also 1 mL of nutrient solution, 2 mL of effluent from ZAB and 2 or 6 drops of nitrification inhibitor ATU (5 g/L). 1 g/L phosphorous buffer at pH 7 was prepared from phosphoric acid and NaOH. Nitrogen stock solution of 5 g/L was prepared from urea. 3 NaOH pellets were added to each rubber sleeve to adsorb the forming CO<sub>2</sub>. Bottles were closed with the measuring head, transferred

to incubator, after which the measurement was started. Incubation time was 7 days and temperature 30°C. Results are reported as BOD<sub>5</sub> values.



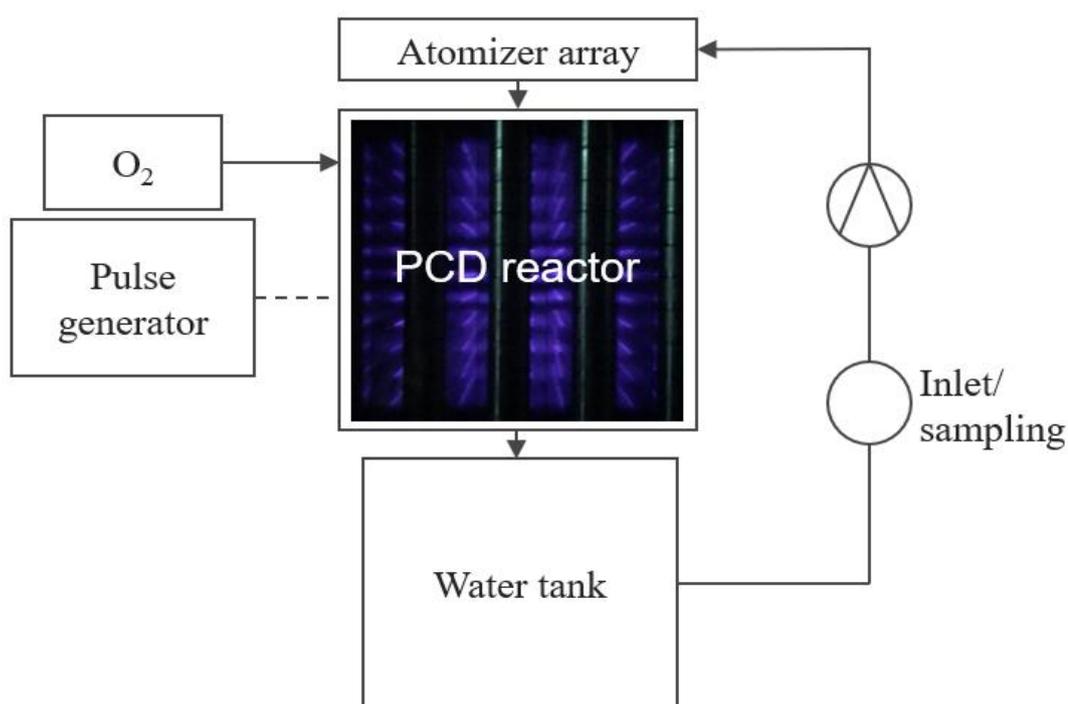
**Figure 7** OxiTop® measurement set with magnetic stirring platform, sample bottles and measuring heads for aerobic BOD studies.

#### **6.4 Oxidation with pulsed corona discharge treatment**

Oxidation as a potential pre-treatment option for biochemical wastewaters was tested with PCD. Method was chosen in order to convert soluble recalcitrant organic compounds, mainly lignin, to more readily biodegradable form to increase BOD<sub>5</sub> value and hence total biodegradability (BOD<sub>5</sub>/COD ratio). Piloting of PCD was performed with Flowrox Corona® piloting unit operated by and in the premises of Wapulec Oy. Three test runs were planned for ash containing and wood handling streams and their diluted mixture to compare treatment of smaller, concentrated streams and larger, less concentrated mixture stream. Fresh sample was collected for the trials with the idea that it would be better than frozen sample. However, it was not representative because of pH and concentration differences compared to earlier sample probably due to process operation and sampling issues. Minimum sample volume for a PCD test was 50 L and there was enough old sample for one test. Therefore, clarified

portion of wood handling stream and older sample of ash containing stream diluted by half were tested.

The flowchart of the pilot unit is shown in Figure 8. The tests were performed in an oxygen atmosphere where 60% oxygen flowed in to the reactor. The sample was circulated on top of the unit, from where it was distributed in the plasma zone by means of sprayers. The nominal power of the pulse generator was 250 W. Energy doses were 0.5, 1, 3, 6 and 10 kWh/m<sup>3</sup>. For diluted sample, the energy doses were halved to correspond the right level and one extra test point, 8 kWh/m<sup>3</sup> to accord energy dose of 16 kWh/m<sup>3</sup> was run. After each dose, pulse generator was stopped, and the water was allowed to mix for five minutes before sampling. The pH, temperature and conductivity were measured from the samples on site. Experimental data from PCD pilots can be found from Appendix III Tables I and II. Reference and test samples were determined later in the UPM NERC laboratories for COD, TOC, lignin concentration and whole UV-Vis spectrum, carbohydrates, carboxylic acids and furans. From wood handling sample extractives were also analysed. BOD<sub>7</sub> ATU was determined by Saimaan Vesi- ja Ympäristötutkimus Oy. Results were converted to BOD<sub>5</sub> values with conversion factors determined from 24-day biodegradability tests.



**Figure 8** Flowchart of PCD pilot unit and glowing plasma zone inside the PCD reactor.

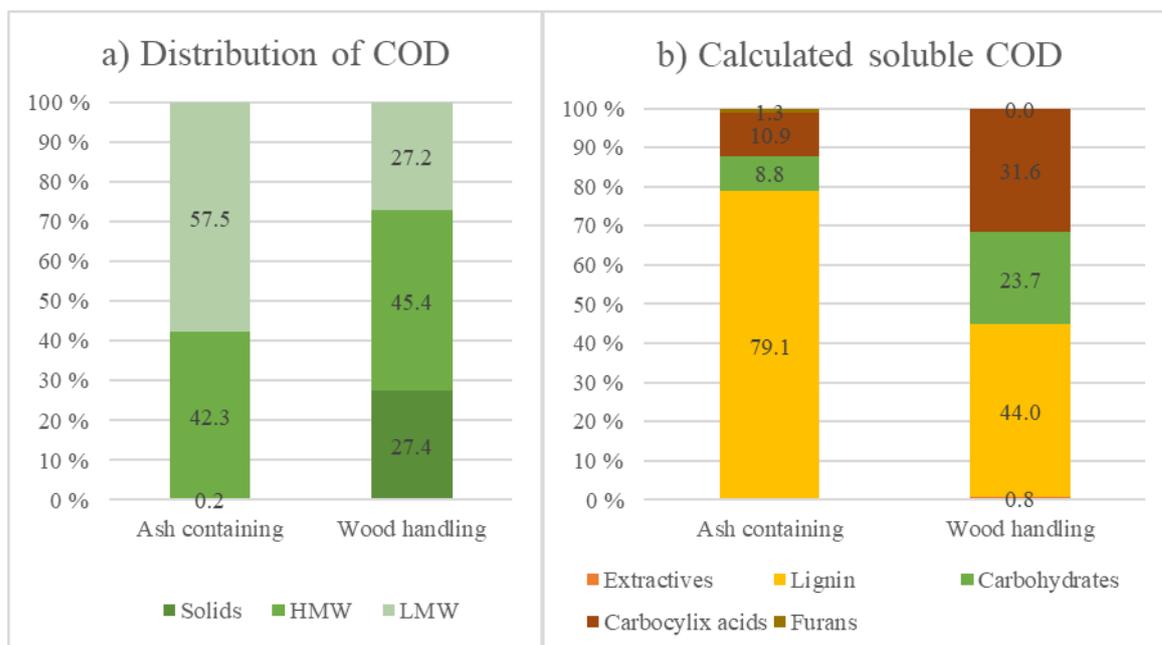
## 7 RESULTS AND DISCUSSION

### 7.1 Characterization and pre-treatment need

#### 7.1.1 COD composition

Samples representing ash containing and wood handling streams were both concentrated having total COD concentrations of 6910 and 5990 mg/L, respectively. COD in ash containing stream is almost entirely (99.8%) in dissolved and colloidal form. More than half of it, 57.6%, was determined as LMW compounds. Largest COD fraction in wood handling stream sample in turn was determined as HMW compounds, forming 45.4% of total COD. UF is expected to retain polymeric and colloidal compounds having molecular mass over 2 kDa like carbohydrates and lignin in wood-based streams. Oligomeric degradation products, sugars, extractives and multivalent ions smaller than 2 kDa can pass through. (Yousefian, 2006)

COD composition is presented in Figure 9 a) as COD fractions based on molecular mass and in b) as calculated COD component fractions. Inconsistency in HMW fraction and amount of lignin was discovered between streams. The preceding process, which can result in different degradation products, is the most likely contributing factor. When comparing analysis results, differences can be formed due to component and further membrane characteristics. Moreover, interference of COD measurement can be caused by chloride and reduced inorganic species. For example, ferrous iron, sulfide, manganous and manganese are oxidizable with dichromate under the test conditions, but these are less unlikely reasons in this case. (APHA, 2018)



**Figure 9 a)** Contribution of solids, HMW and LMW fractions load to COD and **b)** share of organic compounds as calculated COD. Extractives were not determined from the sample of ash containing stream.

For ash containing stream, calculated COD (6960 mg/L) from component concentrations agreed well to the measured COD value (6910 mg/L), resulting only 1% difference. The dominant component determined was lignin (79%). According to COD fractionation results it can be assumed that the residual lignin in the sample is cleaved. On the other hand, one can also question the validity of analysis method and COD conversion factor for this sample. Handling and different conversion processes yield different type of lignin. Also, UV-Vis is not unambiguous, since other compounds like proteins can have adsorbance peak at 205 nm (Anthis&Clare, 2013).

Sample of wood handling stream was more difficult to analyze due to the colloidal fraction. Calculated value (2750 mg/L) was 20% smaller than measured COD (3450 mg/L) from clarified sample. Difference is more likely affected by sample filtration with 0.45  $\mu\text{m}$  filter before component analyses and unanalyzed compounds like uronic acids for example. Comparison to the COD fractionation in turn would correspond well to the fact that lignin and hemicellulose would be in the HMW fraction and carboxylic acids in LMW fraction. As could be expected from the degradation of structural components of wood, most abundant carboxylic acid in both samples was acetic acid and carbohydrates glucose and fructose.

Total COD/TOC values for ash containing and wood handling streams were 3.1 and 4.1, respectively. Ash containing stream corresponded well to the distribution of chemical industry COD/TOC ratios. Ratio of wood handling stream was higher than the average for chemical industry wastewaters, but soluble COD/TOC value (3.0) fitted well to the range. (Brinkmann *et al.*, 2016) Total COD of the anaerobic effluent was 160 mgO<sub>2</sub>/L, from which only 75 mgO<sub>2</sub>/L was soluble. Over half of the determined COD resulted from the anaerobic granules. Measured BOD<sub>5</sub> was 46 mgO<sub>2</sub>/L with standard deviation of 2.6. Soluble COD load expected to continue to the aerobic treatment is low compared to the flow of this stream. Equally, the COD of waste alkali stream (260 mg/L) represents a small COD load compared to the total COD load caused by the from the biorefinery wastewaters.

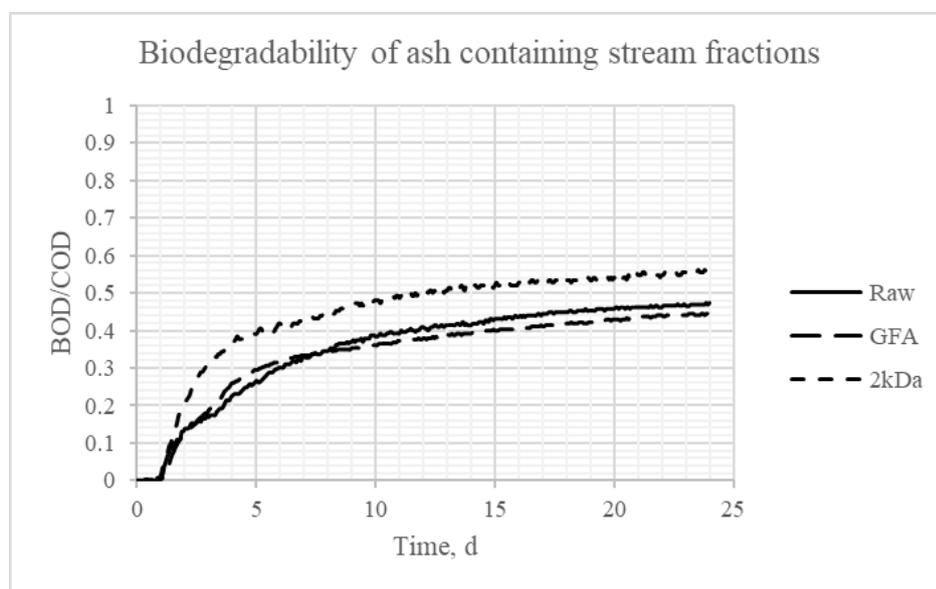
#### 7.1.2 Aerobic biodegradability and treatability

Because streams end up to biological treatment, their biodegradability is largely in term of treatability. Biodegradation tests showed that ash containing and wood handling streams can be suitable for aerobic treatment. As such they are too concentrated but are treatable as a part of larger stream. No acute toxicity or inhibition was observed with raw or filtered fractions. Degradation has started at the same time, under 1-day adaption time and the rate of oxygen consumption is fast in the beginning. BOD<sub>5</sub>/COD values indicate that the biodegradation of wood handling stream (0.32) has progressed faster than the biodegradation of the components in the ash containing stream (0.27), implying higher amount of fast food for microbes. Biodegradation curves are shown in Figures 10 and 11.

Biodegradability as ratio of BOD<sub>24</sub>/COD for raw ash containing stream was 0.47. Therefore this stream is considered to be slowly biodegradable. LMW fraction had higher biodegradability value of 0.56. The increase in biodegradability can be due to larger share of carboxylic acids in that fraction, because they are readily biodegradable. Color was reported to be removed visually. As component analysis showed, recalcitrance and color could be derived from soluble lignin and its fragmented portions. On the other hand, lignin adsorption into sludge would improve treatability, but it is controlled by hydrophobic interactions and surface charges. Lignin with a negative surface charge does not adsorb to biosludge and thus it passes through a bioreactor (Toivakainen *et al.*, 2017). Conducted

biodegradation tests did not take into account of this phenomenon and total removal rate is difficult to estimate. From total dissolved COD, 12% was calculated as HMW biodegradable COD, 30% HMW non-biodegradable COD, 32% LMW biodegradable COD and 25% LMW non-biodegradable COD.

Since biodegradability of dissolved compounds should be closer to 0.8, this stream requires pre-treatment step. Theoretically the removal of HMW compounds as a pre-treatment for example with coagulation/flocculation or UF might not result in high COD removal (42%) nor would it improve biodegradability enough. If other membrane processes are considered, nanofiltration in turn could remove all other pollutants except monovalent ions and volatile acids. This kind of treatment might be oversized as a pre-treatment before biological treatment, but as an advantage could already enable waste stream recycling and savings in water consumption. Suitable pre-treatment before biological treatment to selectively remove the soluble lignin might be adsorption or precipitation. On the other hand, oxidation processes could be used to convert those compounds more biodegradable.

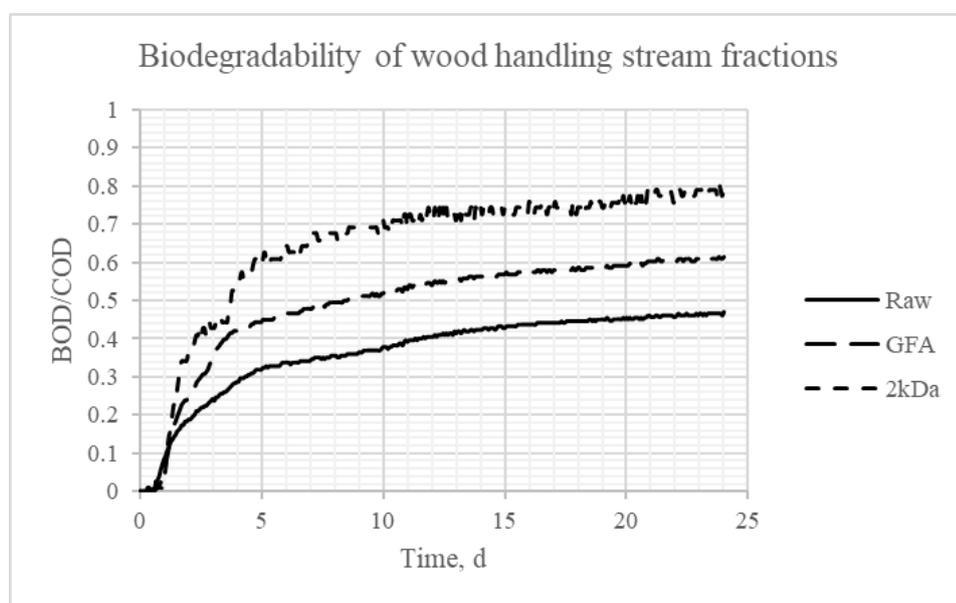


**Figure 10** Biodegradation curve of raw and filtered ash containing stream.

With wood handling sample more clear differences between raw and filtered fractions were observed. Biodegradability increased from 0.47 first to 0.61 in microfiltered sample and finally to 0.81 in LMW fraction. This supports well the component analysis of the sample and beech showing low amounts of toxic and recalcitrant extractives and degradation

products. From total dissolved COD, 31% was calculated as HMW biodegradable COD, 31% HMW non-biodegradable COD, 30% LMW biodegradable COD and 7% LMW non-biodegradable COD.

The removal of particulate matter and HMW fraction could result over 70% total COD removal and remaining soluble contaminants would have readily biodegradable feature. Therefore, ultrafiltration could be considered as a suitable pre-treatment option to decrease COD load and improve biodegradability. Application of UF would require a rough prescreen to remove largest particulates or module that tolerates solids. High-performance membrane with suitable characteristics and long lifetime should be selected and process conditions need optimization (Kallioinen, 2008). However, lignin, extractives and other compounds typical for biorefinery wastewaters can cause fouling and decreasing permeability with some membranes (Virtanen *et al.*, 2019). Alternatively, coagulation/flocculation with suitable chemical and dose could be applied.

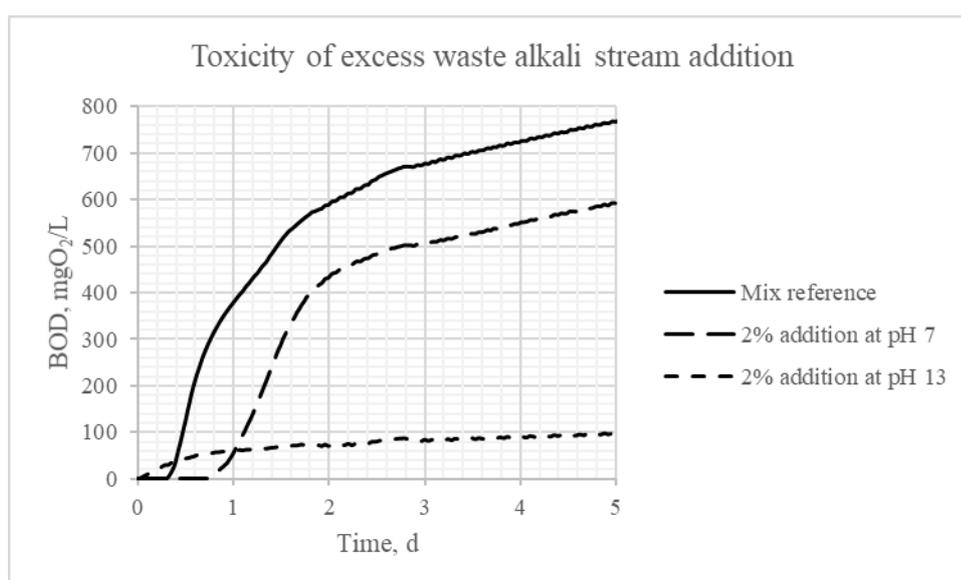


**Figure 11** Biodegradation curve of raw and filtered wood handling stream.

As said, these biodegradation tests were performed with inoculum from paper mill ASP, which is accustomed to degrading wood-derived compounds. In the toxicity test for ZAB microbes, no significant lag or inhibition was observed with the highest sample concentrations (40% and 80%). Biodegradation curves with the mixture sample had even similar pit at the beginning of the curve like can be noticed with sample-specific curves

which may refer to different degrading population. Biodegradation curves are in Appendix II. Blank sample showed no endogenous respiration. No oxygen consumption was measured with diluted samples at concentrations 5%, 10% and 20%. This may be due to too small amount of food for microorganisms to digestate or too small sample volume compared to expected measuring range. The larger proportion of gas phase in the sample bottle could cause inaccuracy in the pressure measurement. Usually toxicity appear at higher concentration, not lower.

Addition of waste alkali stream with and without pH adjustment showed different kind of effects towards reference mixture sample. Results are shown in Figure 12. With pH adjustment the inhibition was seen as a delayed start of the biodegradation which resulted 23% reduction in final BOD<sub>5</sub> value. This could be due to the fact that as a result of the pH adjustment the aluminum precipitated, and the precipitate interfered with the activity between substrates and microorganisms in flocs. As could be expected, strongly alkaline pH was shown as persistent toxicity, decreasing the BOD<sub>5</sub> value by 87%. Thus, the addition of a tested component can cause inhibition for a variety of reasons. All of the samples in this set had same bumps at times around 1.6 and 2.7 d, which is probably due to uneven temperature. These biodegradation curves are good basis for the introduction of the method and interpretation of results in the future to UPM NERC.



**Figure 12** Effect of 2% waste alkali stream addition to degradation of mixture sample.

### 7.1.3 Inorganics

Based on the calculations from metal concentrations, flows and dilution factors, all heavy metal concentrations were under the stricter limit for mixing requirements in the combined stream. No need for heavy metal removal before discharge to ZAB was thus considered. Nickel and zinc concentrations were closest to the legal limit and if changes in compositions or flows occur, these parameters should be monitored again. Tin was found in elevated concentration (40.6 mg/L) compared to the limit (0.2 mg/L) from waste alkali sample but due to dilution effect it does not cause a need for action.

For sulfate, no legislative or additional limit has been set, since it is not a prioritized polluting substance. According to Finnish Water Utilities Association (2018) sulfate limit value for discharge to sewers is usually 400 mg/L. If this kind of level will become to be applied, biorefinery wastewaters need pre-treatment for sulfate removal. Then methods such as distillation, ion exchange, lime precipitation or membrane processes need to be considered.

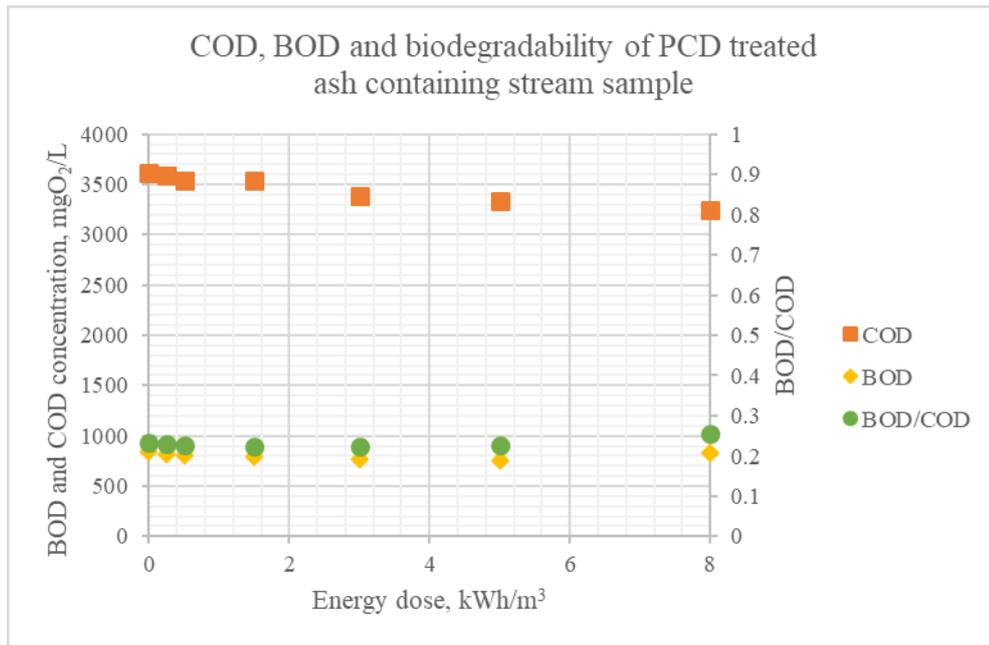
As from the inorganic analysis results can be seen, nutrient amounts in relation to COD concentrations are not enough to cover the nutrient need for activity and growth of microorganisms. Total phosphorus content in ash containing and wood handling streams were 24 and 16 mg/L, respectively. Moreover, total nitrogen results, 90 and 13 mg/L lead to overestimation of bioavailable nitrogen, since greater part is expected to be organically bound. Therefore, these streams require addition of phosphorous and nitrogen before discharge to bioreactor. It is typical for high organic load wastewaters from pulp and paper mills. However, the actual supplement requirement at ZAB depends on the content of other wastewaters, so these calculations are not discussed in more detailed in this thesis.

## **7.2 Performance and suitability of PCD as a pre-treatment**

### 7.2.1 Effect of PCD treatment on biodegradability

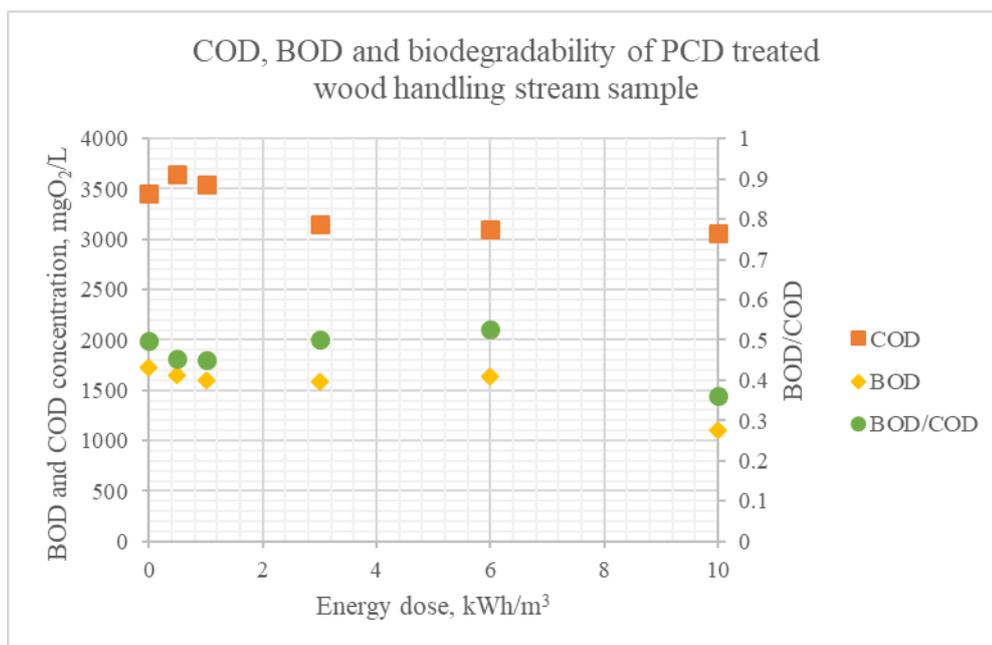
PCD treatment of diluted sample of ash containing stream did not improve biodegradability. BOD value did not practically increase at all. Deviation between samples could even be explained as measurement uncertainty ( $\pm 37\%$ ). Ratio of BOD<sub>5</sub>/COD remained near 0.25 in

each experimental point. Rise of few decimals with the highest energy dose was mainly due to decreased COD value. Achieved COD reduction was 10.2%. Results are presented in Figure 13 as a function of energy dose. Since oxidation processes are not selective, removal of easily oxidizable compounds and formation of oxidation products could keep BOD from changing.



**Figure 13** COD, BOD<sub>5</sub> and biodegradability of ash containing stream sample as a function of energy dose.

Biodegradability (measured as BOD<sub>5</sub>/COD) of the PCD treated sample of wood handling stream first decreased with low energy doses due to increase in COD. The phenomenon is common with oxidation processes as the oxidation reactions generate oxidation products, which are oxidizable in the measurement analysis unlike the initial compound. Biodegradability reached its highest value with energy dose of 6 kWh/m<sup>3</sup> because of decreased COD concentration. After that COD remains steady even as the energy dose increases. Achieved COD reduction was 11.3%. With the highest energy dose, all oxidation was consumed to remove BOD from the perspective of biodegradability, which decreased finally below the initial value. Results are presented in Figure 14 as a function of energy dose.



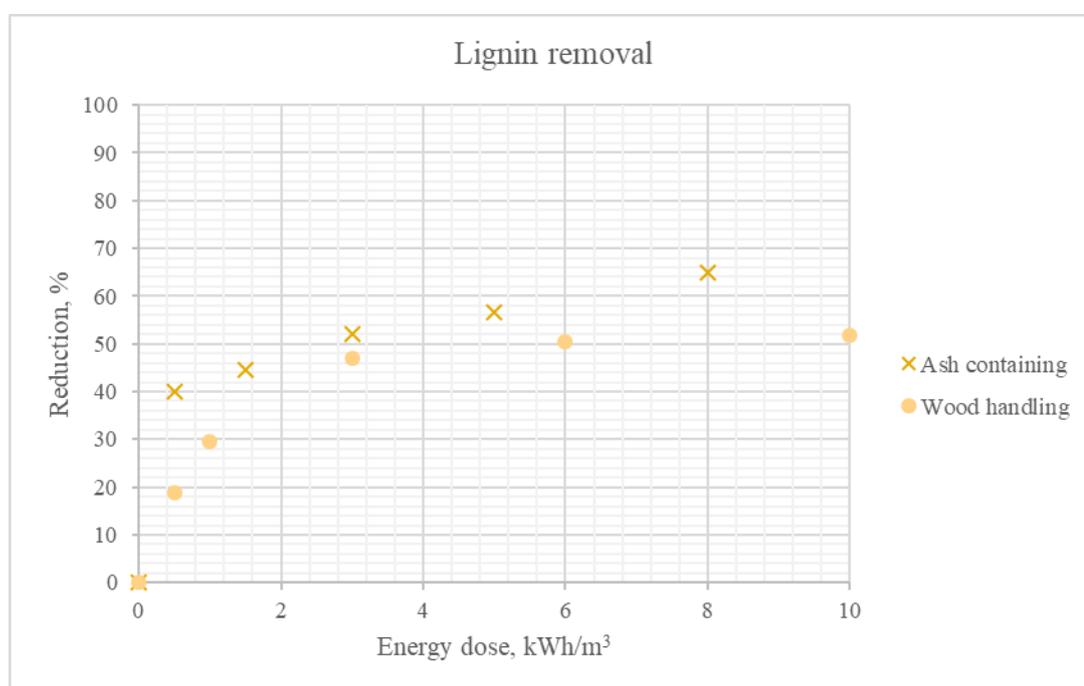
**Figure 14** COD, BOD<sub>5</sub> and biodegradability of wood handling stream sample as a function of energy dose.

Structural changes by oxidation treatment cannot be necessarily seen in the sum parameters especially with complex component composition if partial oxidation of recalcitrant compound has occurred. Interpretation of only COD and BOD results provide very little information about the oxidation reactions that have taken place. TOC results could have been showing mineralization as decreased organically bound carbon, but no significant trend was discovered. Values changed up or down within 100 mg/L of the initial value. Small changes in TOC results are however typical, since total mineralization by AOPs is assumed only for simple compounds as Arola *et al.* (2018) observed, too. Total mineralization is expected with AOPs only for simple compounds. Decrease in pH for ash containing stream however indicate that acidic oxidation products have been formed.

### 7.2.2 Component specific results and oxidation reactions

Lignin analysis showed lignin reductions of 65% and 52%. Lignin removal as a function of energy dose is presented in Figure 15. Lower lignin reduction in wood handling wastewater sample despite higher energy dose can be due to acidic pH, since oxidation of lignin is found to be more efficient in alkaline pH. Efficiency has been reported to increase also with increasing lignin concentration. PCD treatment of lignin yields aldehydes, which are further

oxidized to carboxylic acids by hydroxyl radicals. (Panorel, 2014; Sokolov, 2019) Ozone does not attack on aldehydes and carboxylic acids (Sillanpää *et al.*, 2017). Also, color, which is associated generally to lignin, was detected to lighten with processing. Color could not be measured due to turbidity, but change is presented in Appendix III Figures 2 and 3. Visually it not seemed to correlate with the lignin concentration, since color change was more evident between the two last experimental point. Contrariwise lignin removal was higher with lower energy doses and slowed towards further treatment. Color change could thus express structural change of lignin or other compounds adsorbing at the same wavelength.

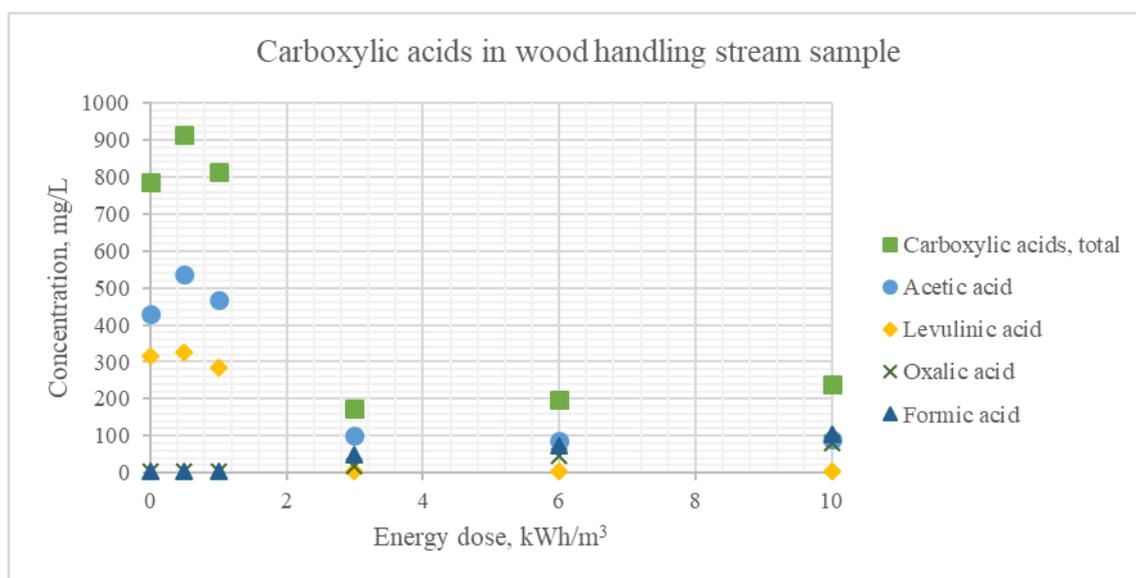


**Figure 15** Lignin removal as a function of energy dose.

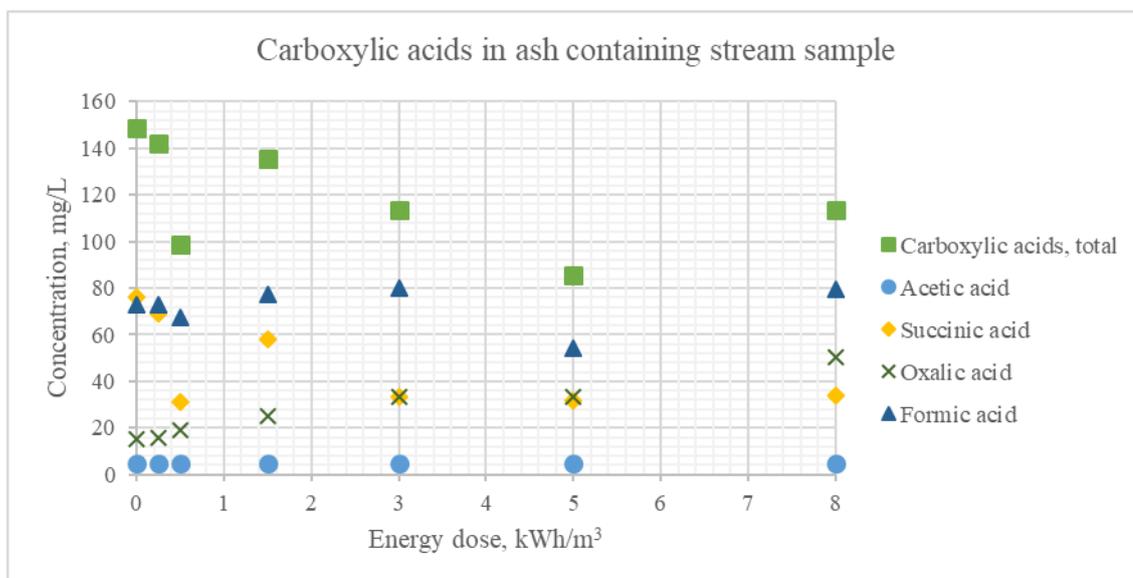
In addition to lignin concentration, which was determined at wavelength 205 nm, whole spectrum from UV-Vis from wavelengths 190-700 nm was detected. In samples of wood handling stream the significant change during PCD treatment was decrease of peak at 280 nm. These spectra can be found in Appendix III Figures 4-6. Presence of unsaturated substituent like carbonyl group and double bond on  $\alpha$ -carbon of the lignin side chain can contribute to the peak at 280 nm. These groups are also responsible for lignin color. (Jablonský *et al.*, 2013) It seems that these linkages have been broken, cleaving lignin derivatives further on.

For ash containing stream, similar decrease was noticeable with peaks at 340 and 360-370 nm. Also, the first wide peak seemed to narrow due to decrease around 240 nm. These spectra can be found in Appendix III Figures 7-10. Peaks at 340 nm indicate conjugated structures like double bond between  $\alpha$ - and  $\beta$ -C and carbonyl groups in the side chains of lignin. Peak at 360-370 nm is associated with conjugated phenolic units. (Jablonský *et al.*, 2013)

Total carboxylic acid concentration in wood handling stream increased with lowest energy dose of 0.5 kWh/m<sup>3</sup> as Figure 16 shows. It is due to increase of acetic acid derived presumably from lignin degradation. After this carboxylic acid concentration drops below 200 mg/L due to oxidation of larger carboxylic acids. Smaller carboxylic acids oxalic and formic acids are the last degradation steps before mineralization. These are more recalcitrant to oxidation. Since oxidation of organic compounds occurred, concentration of oxalic and formic acid increased with PCD treatment. Same type of increase with oxalic and formic acids is seen with ash containing stream as can be seen in Figure 17.



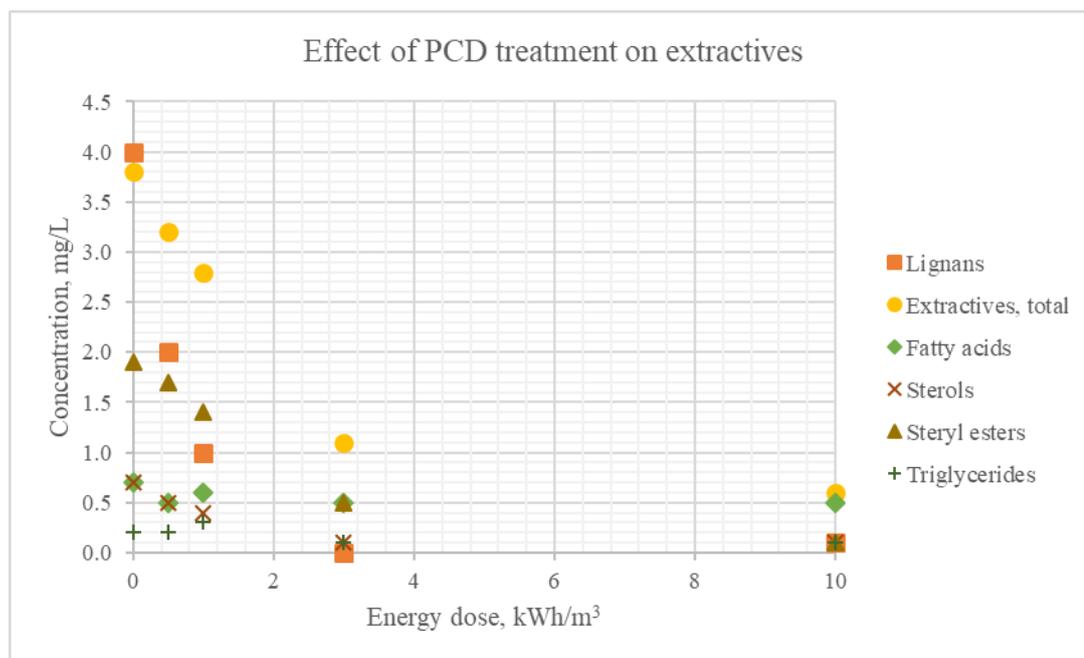
**Figure 16** Carboxylic acids in wood handling sample as a function of energy dose.



**Figure 17** Carboxylic acids in ash containing stream as a function of energy dose.

Carbohydrate content remained unchanged in wood handling stream despite PCD treatment. These results were expected since sugars are not chemically oxidizable. Decrease in total concentration of carbohydrates in the ash containing stream could be due to the longer storage time between test runs and analysis. Wood handling samples were analyzed the next day and ash containing samples week after, during which other type of degradation may have occurred. These results can be found from Appendix III Tables III and IV.

In spite of low concentration of extractives, PCD treatment was found to be efficient for their degradation. Extractives concentration as a function of energy dose are presented in Figure 18. Especially for polyphenol lignans, oxidation has been destructive resulting in 98% reduction. Lignans are dimeric compounds containing same type of monomers than lignin. Also, with steryl esters and sterols decrease in concentration is obvious, 95% and 86%, respectively. With fatty acids some changes with low energy doses were observed, but clear degradation was not reached. Interpretation of triglycerides is uncertain due to the low initial concentration. As these results suggest, oxidation is effective for degradation of extractives and treatment of more toxic streams containing for example phenolic tannins could be considered with PCD. For toxic streams simultaneous detoxification and partial oxidation as a pre-treatment could help the following biological treatment.



**Figure 18** Extractives concentration in wood handling stream as a function of energy dose.

Unfortunately, due to the lack of sample, comparison for treatment of concentrated streams versus more diluted combined stream was not able to be accomplished. Anyway, the determination of optimal energy dose was difficult due to various results. Because biodegradability was kept as a measure of success, no conclusion can be drawn from it. If optimizations were made based on the lignin and extractives results, energy dose below 4 kWh/m<sup>3</sup> could be practicable. But if contributing factors were oxalic and formic acid concentrations and color removal, higher energy doses would be applied. To improve efficiency, streams with easily biodegradable feature should bypass this kind of treatment because of the non-selectivity of hydroxyl radicals.

### 7.2.3 Reasons restricting effectiveness

Based on the above results, partial oxidation has occurred, but no positive results are seen in the biodegradability measurements. One contributing factor can be the relatively high BOD load in the samples, although BOD/COD ratio is low. This is the downside of using hydroxyl radical with un-selective nature as a pre-treatment. Perhaps the results would had appeared in the COD fractionation as an increase in LMW fraction, but these determinations were not conducted during this work. Clear correlations between the results were difficult to find probably due to the complexity of the chemistry of the treated samples. At least with

ozonation, LMW fraction was increased due to degradation of inert soluble COD to biodegradable form. (Fanchiang *et al.*, 2009) Biodegradation rate is expected to increase with decreasing particle size, but chemical composition affects also to the rate (Yousefian, 2000). It is also suggested that ozonated samples need more accustoming time in the BOD test, and thus BOD<sub>10</sub> would be more recommended for pre-treated samples (Beltrán, 2003).

Since PCD method is based on electric pulses discharged into the reactor, high electrical conductivity of treated water can cause harm. The first drawback is linked to energy consumption. Energy is wasted in the (heating of) water instead of oxidants formation. Surface discharges can also appear as sparks in the plasma reactor. These surface discharges were witnessed with high conductivity ash containing stream. There are some device technical improvements related to reactor structure and water distribution system available that can diminish this phenomenon. Also related to energy consumption, for concentrated streams applies the rule that the higher concentration, the higher energy is needed to achieve more profound degradation. Moreover, factors like pH and presence of radical scavenger species (carbonate and bicarbonate ions) affect the performance (Ajo, 2018).

With the tested samples, heavy foaming was generated with low energy doses. Foaming was detected to decrease when more ozone was formed (detected when excess ozone come out from the outlet pipe of the reactor). Evidence on formation is shown in Appendix III Figure 1. It is possible that the foam affected the volume flow, according to which the processing time required for the energy dose was determined. Furthermore, foaming is due to presence of surface-active components in the treated water. In these samples the surfactants are more likely wood extractives, lignin derivatives and proteins. Since formation of degrading radicals are formed and act in the plasma liquid interface, surface chemistry influences performance. Some classes of hydrophobic molecules are said to restrict penetration through plasma-liquid interface. Surfactant can attract to the interface. (Bruggeman *et al.*, 2016)

### **7.3 Risk assessment for biorefinery wastewaters**

Many risk factors are associated with the uncertainty of wastewater generation. The main targets are not to exceed given flow and load limits and mixing requirements. Equally important is not to hinder the biological treatment so that sufficient overall COD reduction

can be obtained. Industrial discharges are hard to predict in the first place. In normal operation content and load may be well known and constant but process disturbances and special situations can make a difference. Changes in the flow during start-up, cleanup and shutdown are difficult to estimate. (Tchobanoglous *et al.*, 2003) Overload of wastewater or sudden problem should be prepared with precautionary tanks or pools. In the startup of new biorefinery, there might form intermediate products of a quality that cannot be used forward in the process and end up in wastewater streams. Biodegradability of such compounds has not been not tested, but for the most part at least sugars are readily biodegradable.

The raw material has big influence on the wastewater composition in each process step. As said, other hardwoods than beech can be also used. Even in the tree species belonging to same family (*Fagaceae*) hemicellulose, lignin and extractive composition can vary greatly. Beech was discovered to be quite less toxic by means of amount of extractives and acidity. Oak for example has higher amount of condensed tannins and total extractives content compared to beech. Oak bark water extract may also be more acidic. (Kettunen, 2006) For debarking waters low load to biological treatment is important in terms of biological activity (Saunamäki, 1994). According to estimates, debarking effluent flow is 12% of total wastewaters originating from biorefinery. This portion is further reduced to less than half when streams are discharged to ZAB. Dilution factor should be enough to eliminate possible toxic effect present in the debarking water. With debarking plant type, operation and water recycling the quantity and quality of waste water can be affected. Still the fact remains that daily and seasonal fluctuations can cause challenges. More important, removal of inorganic impurities and pieces of bark before discharge to ZAB is essential.

The addition of anaerobic pre-treatment to the ZAB is essential for the capacity of the centralized treatment plant, since majority of discharged wastewater as flow and COD load from biorefinery are treated with it. Anaerobic processes are however more sensitive to disturbances than aerobic systems. Precise operation and control of anaerobic process is particularly important. On the basis of performed pilot tests, achieved COD reduction has been really promising, even 98%. Nevertheless, it is known that the influent to anaerobic reactor contains for example furfural that can be inhibitor at high concentrations but does not hinder degradation at low concentrations. With substantially lower COD reductions below 82% alternative or additional treatment methods should be used so that the load going

to the aerobic treatment does not become too great. Other more expected harms derived from anaerobic effluent are odours. It originates from hydrogen sulfide when sulfur compounds are reduced by microorganisms. Even at low concentrations 0.0005-5 ppm (upper limit referring for 8 h working conditions), smell is noticed unpleasant or familiar to a rotten egg. Higher concentrations than 5 ppm it causes even health hazard. (Finnish Water Utilities Association, 2018)

Dilution factor for aerobic treatment obtained from the joint treatment is good for toxicity point of view, but it can make things more difficult with persistent compounds. The concentration of non-biodegradable compounds can drop below detection limit, which makes the control of treatment performance impossible. Problems can occur at the bioreactor or in the receiving waters. At the treatment plant, some compounds can inhibit the nitrification step even at low concentration, and recovery of nitrification step can take time several weeks even (Brinkmann *et al.*, 2016). Reaching the final discharge limit may become more challenging and without sufficient treatment, persistent compounds end up to receiving waters and water cycle and can bioaccumulate. One potential cause for eutrophication is the organically bound nitrogen, which is not bioavailable during wastewater treatment, but can after further degrading be released in the water system. AOX chemicals are usually associated with pulp and paper mill effluents and their environmental impacts have been widely discussed. These compounds are not generated in biochemical processes, since chloro-compounds are not used, but due to remaining organic compounds AOX chemicals could be formed in disinfection step. Therefore, disinfection should not be applied at any point in the water treatment process to stream involving remaining organics prone to react with chlorine.

If excess sulfates are not removed, freshwater organisms can be harmed (Brinkmann *et al.*, 2016). Average sulfate concentrations below 2 g/L in treatment plant effluents are reported by Brinkmann *et al.* (2016). This concentration is not exceeded even in the influent of UPM wastewaters to ZAB. Sulfate reduction in biological treatment plant is in general low. High sulfate and sulfite concentrations in wastewater can cause problems already in the treatment plant by concrete corrosion. Under certain conditions, sulfates intrude into and reacts with concrete causing swelling of concrete. Also, chloride, magnesium, ammonium, low pH below 6 and high temperature can predispose to corrosion. (Finnish Water Utilities

Association, 2018) Other substance with detected elevated concentration was sodium. High concentration of sodium is only problematic with drinking water so that should not cause additional risks to ZAB. If necessary, removal of excess sulfate or sodium can be achieved with reverse osmosis, electrodialysis, bipolar membrane electrodialysis, distillation, ion exchange or lime precipitation.

As was found in the PCD treatment of wastewater samples, they contained surface active compounds responsible for foaming. Similarly, these compounds can cause foaming problem in the bioreactor. Biological foam can be more viscous and stronger than foam from synthetic compounds and typically reduce performance of aeration and secondary clarifier (Collivignarelli, 2020). Foaming can be reduced in the treatment plant by adding anti-foaming substances or water sprays.

Discharge of liquid aluminum salt could result in aluminum precipitation in changing conditions of pH and temperature. Amorphous precipitate is prone for scaling, if mixing is not continuous and flow big enough. Aluminum sludge moreover increases the amount of sludge. It hampers sludge settlement, aeration by means of toxicity to microorganisms or depletion of oxygen, effluent quality and incineration properties of sludge. (Finnish Water Utilities Association, 2018) On the other hand, feeding liquid alkaline alumina to activated sludge plant is reported to have operational benefits. For example, improved suspended solids removal in secondary clarifiers, easier sludge handling and volume index control has been noted. (Lenhart&Cagle, 1975) If water contains high amounts of salt already, addition of aluminum salt is not necessarily suitable. (McEwen, 1998)

#### **7.4 Further research**

Especially for the wood handling stream removal of solids and colloids play an important role in COD reduction. It is not yet known how efficient the flocculation and flotation procedure at ZAB is for these streams. The dilution effect on full scale can affect the removal rate compared to a simple jar test, which can be conducted for small sample volumes. If the existing precipitation agent is discovered to be not suitable and efficient enough for this type of wastewaters it should be inquired, if the existing process could be enhanced with other

chemicals. Alternatively, separate treatment of concentrated stream is necessary at the place of occurrence.

The role of waste alkali stream in the wastewaters could be coupled to the solids and colloids removal. It could be used as an efficient coagulant. But this thought needs more detailed clarification if it is economically and operationally realistic to execute.

The biodegradation tests conducted in this work are adequate to estimate the COD composition of the streams. Hydraulic retention time and other plant-specific factors affect the actual COD reduction. Better estimation describing the total TOC eliminability in the treatment plant is however achieved with the DIN 9888 test performed at the actual site. This test can take into account also the abiotic loss of organic load attained for example with adsorption to the biomass. This is also the official legal proof if pre-treatment is needed before discharge to centralized treatment plant. Also, biodegradability of intermediate products and new type of streams can be performed with Oxitop® method.

When the need of pre-treatment is certain, selection of suitable pre-treatment method is made stream-specific. In this work, PCD oxidation was tested but treatment did not improve biodegradability with the chosen measurement method. Tests with subsequent biological treatment step should be conducted if actual effects reached with partial oxidation with this treatment is wanted to find out. Optimum energy dose should be discovered for requisite pre-treatment and comparison with other possible methods conducted. More selective oxidation of remaining lignin double bonds could be achieved with ozonation, but cost-effectiveness and ease of operation might suffer. Also use of profitable adsorbent might be conceivable option. Application of membrane processes could be feasible for simultaneous removal of excessive COD and salts, enabling water reuse and overall wastewater reduction.

## **8 CONCLUSIONS**

The selection of proper wastewater treatment method depends on the type of wastewater and requirements for the quality of treated water. New wastewaters derived from wood handling and biochemical processes described in this work, are destined to be discharged into centralized biological wastewater treatment plant. Requirements for load and elimination of

organic content cause need for pre-treatment. Limitations concern especially toxic heavy metals and persistent or slowly biodegradable organic compounds. The focus was in the biodegradability of wastewater streams. OxiTop® method was found to be simple and informative tool for determination of aerobic aqueous biodegradability.

Based on the conducted wastewater characterization, streams containing high concentrations of organic load do not cause acute toxicity or retard the activity of aerobic microorganisms. For now, for wastewater stream derived from wood handling of beech, removal of solids and colloidal COD is enough before aerobic treatment, since soluble fraction was determined to be easily biodegradable. If whole cost-efficiency is considered or preliminary reduction in total COD load to ZAB is wanted, it should be resolved whether removal of solids is more efficient and profitable as separate concentrated or diluted combined stream and with which chemical.

The ash containing stream displayed less biodegradable feature and higher portion of soluble COD load. There is a possibility that lignin and its derivatives are adsorbed into biosludge which results in high enough COD removal. However, it is also very likely that the existing treatment process is not efficient in degradation of recalcitrant compounds. For this reason, need for additional pre-treatment step to enhance biodegradability was considered realistic. An advanced oxidation process in the form of gas phase pulsed corona discharge (PCD) treatment was found to be a practicable option.

PCD with tests Flowrox Corona® showed that although no mineralization and improvement in BOD<sub>5</sub>/COD ratio occurred, partial oxidation for dominant recalcitrant component, lignin, was achieved. The pH decreased for ash containing stream was confirmed to result in increase in concentration of small carboxylic acid degradation products. Also, for wood handling stream, decrease in concentration of extractives was achieved. These happened oxidation reactions should help the performance of subsequent biological treatment but the extent of such enhancement is not known. It remains to be resolved which would be optimum energy dose and system configuration, if PCD is applied. Because of surface active compounds and high COD concentration, high doses of energy might be needed which reduces cost-efficiency of this method.

Further research is recommended with fresh representative samples and their biodegradability tests to qualify and update the becoming real wastewater composition. It is suggested to collect streams with such different characteristics in terms of biodegradability into separate tanks since they require different kind of pre-treatment. Also, the actual risk factor of high salt concentration and foam potential should be quantified. In addition to organic components, removal of sulfate may require actions. Furthermore, comparison of cost-effectiveness between different pre-treatment methods for removal of soluble non-biodegradable compounds like PCD, membranes and adsorption could be made.

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Complete characterization data

**Table I** Basic characterization results and organic content of samples.

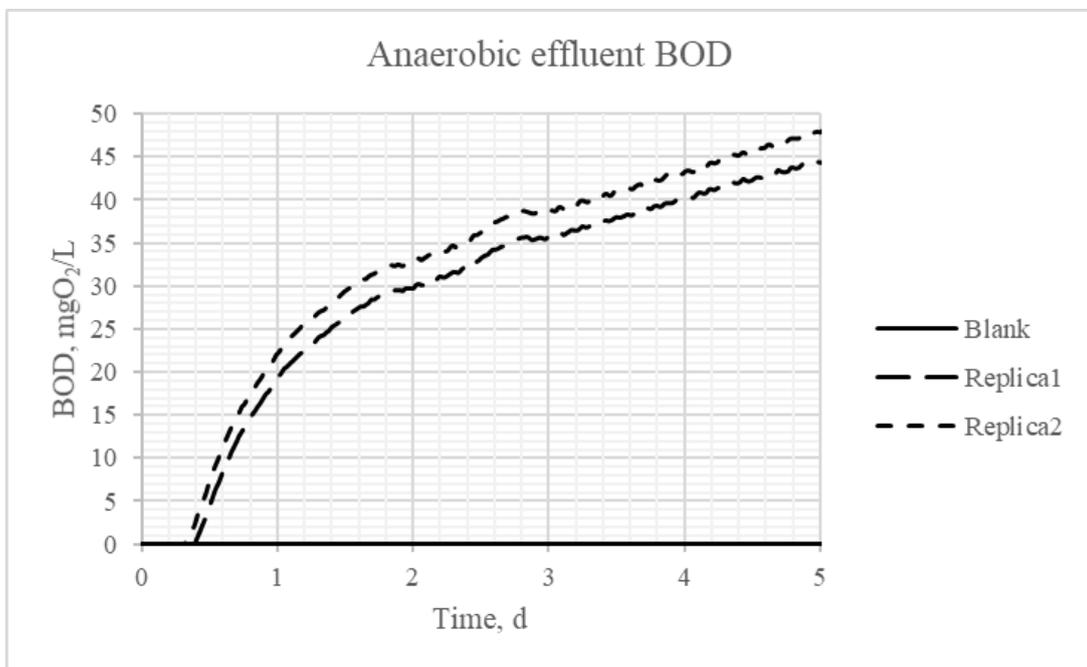
Parameter	Unit	Ash containing	Wood handling	Anaerobic effluent	Waste alkali
<b>pH</b>		9.5	4.0	8.6	12.8
<b>Suspended solids</b>	mg/l		1690	240	
<b>Dry content, 105°C</b>	%	1.6	0.5	0.2	53.0
<b>COD<sub>Cr</sub></b>	mgO <sub>2</sub> /l			160	260
<b>COD<sub>Cr</sub>, filtered sample</b>	mgO <sub>2</sub> /l		3450	75	
<b>TOC</b>	mg/l	2250	1150	40	
<b>Cellobiose, HPLC-RI 2</b>	mg/l	9.1	46.2		
<b>Glucose, HPLC-RI 2</b>	mg/l	233.0	219.8		
<b>Xylose, HPLC-RI 2</b>	mg/l	15.6	9.3		
<b>Arabinose, HPLC-RI 2</b>	mg/l	<5	35.9		
<b>Galactose, HPLC-RI 2</b>	mg/l	39.1	8.7		
<b>Mannose, HPLC-RI 2</b>	mg/l	98.7	<5		
<b>Fructose, HPLC-RI 2</b>	mg/l	122.8	267.6		
<b>Carbohydrates total, HPLC-RI 2</b>	mg/l	509.1	541.2		
<b>Oxalic acid, PDA</b>	mg/l	39.9	<5	<5	
<b>Citric acid, PDA</b>	mg/l	23.8	43.1	<5	
<b>Succinic acid, PDA</b>	mg/l	106.2	<5	<5	
<b>Formic acid, PDA</b>	mg/l	168.9	<5	<5	
<b>Acetic acid, PDA</b>	mg/l	391.3	430.9	<5	
<b>Levulinic acid, PDA</b>	mg/l	<5	313.6	<5	
<b>Carboxylic acids, total, PDA</b>	mg/l	690.1	787.6	0.0	
<b>2-Furoic acid, PDA</b>	mg/l	16.7	<5	<5	
<b>5-HMF, PDA</b>	mg/l	34.6	<5	<5	
<b>Furfural, PDA</b>	mg/l	<5	<5	<5	
<b>Furans, total, PDA</b>	mg/l	51.3	0.0	0.0	
<b>Lignin, soluble, UV 205</b>	mg/l	2895	636	22	
<b>Fatty acids, MTBE+GC</b>	mg/l		0.7		
<b>Resin acids, MTBE+GC</b>	mg/l		0.3		
<b>Sterols, MTBE+GC</b>	mg/l		0.7		
<b>Betulinols, MTBE+GC</b>	mg/l		<0,10		
<b>Steryl esters, MTBE+GC</b>	mg/l		1.9		
<b>Triglycerides, MTBE+GC</b>	mg/l		0.2		
<b>Extractives, total, MTBE+GC</b>	mg/l		3.8		
<b>Lignans, MTBE+GC</b>	mg/l		4		

**Table II** Inorganic content of samples.

<b>Parameter</b>	<b>Unit</b>	<b>Ash containing</b>	<b>Wood handling</b>	<b>Anaerobic effluent</b>	<b>Waste alkali</b>
<b>Total nitrogen</b>	mg/l	90	13	42	
<b>Aluminium, Al, ICP</b>	mg/l	<0.04	1.77	0.153	13800
<b>Arsenic, As, ICP</b>	mg/l	<0.01			<0.75
<b>Boron, B, ICP</b>	mg/l	<0.06	0.192		5.7
<b>Calcium, Ca, ICP</b>	mg/l	0.437	123	95.6	<2.5
<b>Cadmium, Cd, ICP</b>	mg/l	<0.001	0.005	<0.001	<0.10
<b>Cobalt, Co, ICP</b>	mg/l	<0.002			<0.15
<b>Chromium, Cr, ICP</b>	mg/l	<0.01	0.588	<0.01	<0.50
<b>Copper, Cu, ICP</b>	mg/l	<0.003	0.238	0.047	<0.25
<b>Iron, Fe, ICP</b>	mg/l	0.124	7.68	3.59	<0.75
<b>Mercury, Hg, ICP with hydride generator</b>	µg/l		<0.5	<0.5	<5
<b>Potassium, K, ICP</b>	mg/l	11	264	95.2	51.4
<b>Magnesium, Mg, ICP</b>	mg/l	0.205	47.6	15.7	<1.25
<b>Manganese, Mn, ICP</b>	mg/l	0.007	5.15		<0.25
<b>Molybdenum, Mo, ICP</b>	mg/l	<0.002			896
<b>Sodium, Na, ICP</b>	mg/l	4716	10.7	578	119000
<b>Nickel, Ni, ICP</b>	mg/l	0.034	0.478	0.08	<0.25
<b>Phosphorus, P, ICP</b>	mg/l	24.4	16	26.5	<2.5
<b>Lead, Pb, ICP</b>	mg/l	<0.01	<0.01	<0.01	<0.75
<b>Sulphur, S, ICP</b>	mg/l	2586	177	14.3	56.9
<b>Selenium, Se, ICP</b>	mg/l	<0.02			<0.75
<b>Silicon, Si, ICP</b>	mg/l	0.87			
<b>Tin, Sn, ICP</b>	mg/l		<0.01	<0.01	40.6
<b>Zinc, Zn, ICP</b>	mg/l	0.115	0.991	0.459	<0.50
<b>Acetate, IC</b>	mg/l	135			
<b>Formiate, IC</b>	mg/l	101			
<b>Chloride, IC</b>	mg/l	<0.3	14	592	
<b>Sulphate, IC</b>	mg/l	8350	564	33.9	
<b>Nitrate, IC</b>	mg/l	<0.1	155	<0.1	
<b>Lactate, IC</b>	mg/l	304.65			
<b>Phosphate, IC</b>	mg/l	74.8	36.6	41.1	

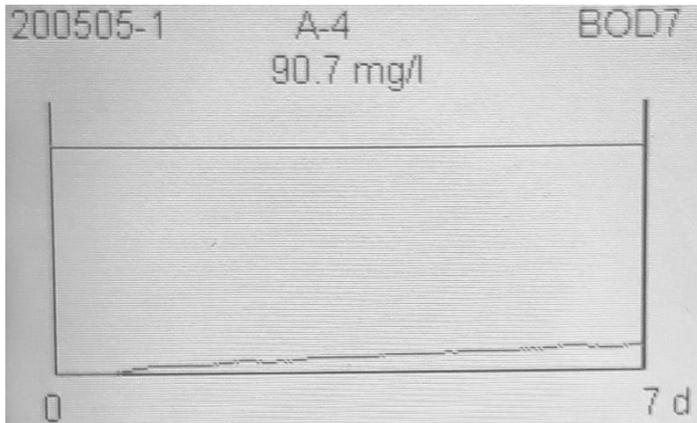
**Table III** COD characterization and BOD data from Toihan Oy. Unit mgO<sub>2</sub>/L.

	Ash raw	Ash GFA	Ash 2kDa	Wood raw	Wood GFA	Wood 2kDa
<b>COD (Hach LCK 514)</b>	6906	6894	3974	5990	4348	1627
<b>BOD<sub>5</sub></b>	1833	2039	1555	1915	1927	965
<b>BOD<sub>7</sub></b>	2283	2302	1690	2050	2077	1070
<b>BOD<sub>24</sub></b>	3261	3070	2235	2820	2668	1310
<b>BOD<sub>5</sub>/COD</b>	0.265	0.296	0.391	0.320	0.443	0.593
<b>BOD<sub>7</sub>/COD</b>	0.331	0.334	0.425	0.342	0.478	0.658
<b>BOD<sub>24</sub>/COD</b>	0.472	0.445	0.562	0.471	0.614	0.805
<b>BOD<sub>5</sub>/BOD<sub>7</sub></b>	0.803	0.886	0.920	0.934	0.928	0.902
<b>BOD<sub>5</sub>/BOD<sub>24</sub></b>	0.265	0.296	0.391	0.320	0.443	0.593

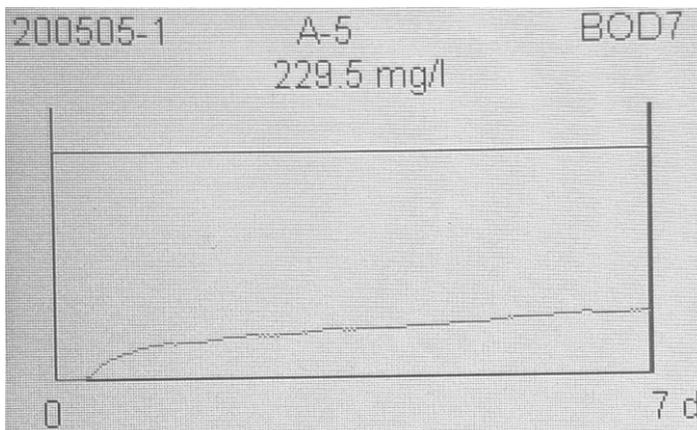
**Figure 1** BOD<sub>5</sub> determination for anaerobic effluent.

## Toxicity measurements

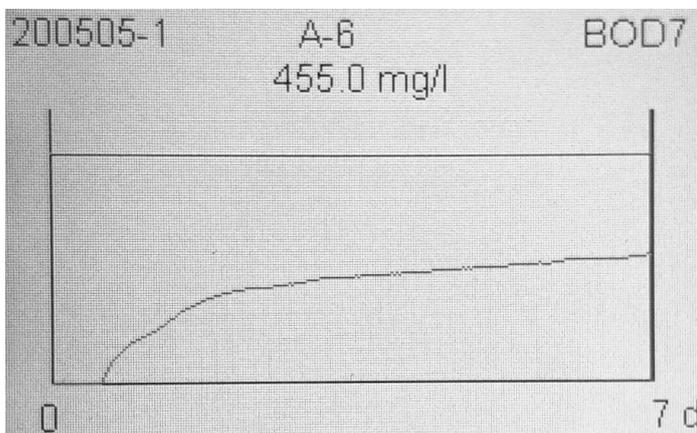
No oxygen consumption in samples 1-3 i.e. blank, 5% and 10%.



**Figure 1** Biodegradation curve of 20% mixture sample.



**Figure 2** Biodegradation curve of 40% mixture sample.



**Figure 3** Biodegradation curve of 80% mixture sample.

## PCD experiment data and results

**Table I** PCD test data with wood handling stream.

Energy dose, kWh/m <sup>3</sup>	Treatment time	Conductivity, mS/cm	pH	Temperature, °C	O <sub>2</sub> , %	Comment
<b>0</b>		1.25	4.0	16.2	72	Low pH, usually easier oxidation of components in alkaline solution
<b>0.5</b>	5 m 33 s	1.43	4.0	17.2	71	
<b>1</b>	5 m 20 s	1.47	4.0	18.6	71	
<b>3</b>	20 m 31 s	1.46	4.0	20.7	71	Ozone concentration clearly increased
<b>6</b>	29 m 31 s	1.54	4.0	23.4	70	
<b>10</b>	37 m 41 s	1.64	4.0	25.9	67	

**Table II** PCD test data with diluted ash containing stream.

Energy dose, kWh/m <sup>3</sup>	Treatment time	Conductivity, mS/cm	pH	Temperature, °C	O <sub>2</sub> , %	Comment
<b>0</b>		9.49	10.4	16.3	66	
<b>0.25</b>	3 m 7 s	9.49	10.3	17.3	65	
<b>0.5</b>	3 m	9.52	10.2	18.0	66	
<b>1.5</b>	11 m 31 s	9.57	10.0	19.6	67	
<b>3</b>	16 m 34 s	9.45	9.5	21.5	69	
<b>5</b>	21 m 7 s	9.63	8.6	23.5	69	
<b>8</b>	30 m	9.65	7.8	25.2	69	The small amount of ozone disappeared very soon after the experiment, i.e. there would still be a lot oxidizing



**Figure 1** Foaming problem (left) and end of foaming when enough ozone was formed (right).



**Figure 2** Color change of wood handling stream sample with increasing energy dose.



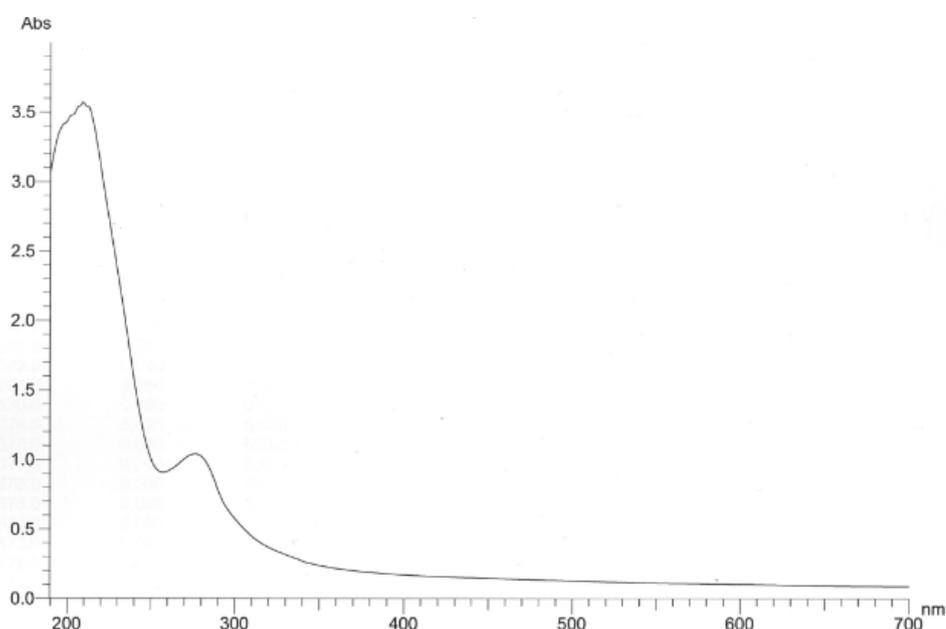
**Figure 3** Color change of ash containing stream sample between reference and after energy dose of 8 kWh/m<sup>3</sup>.

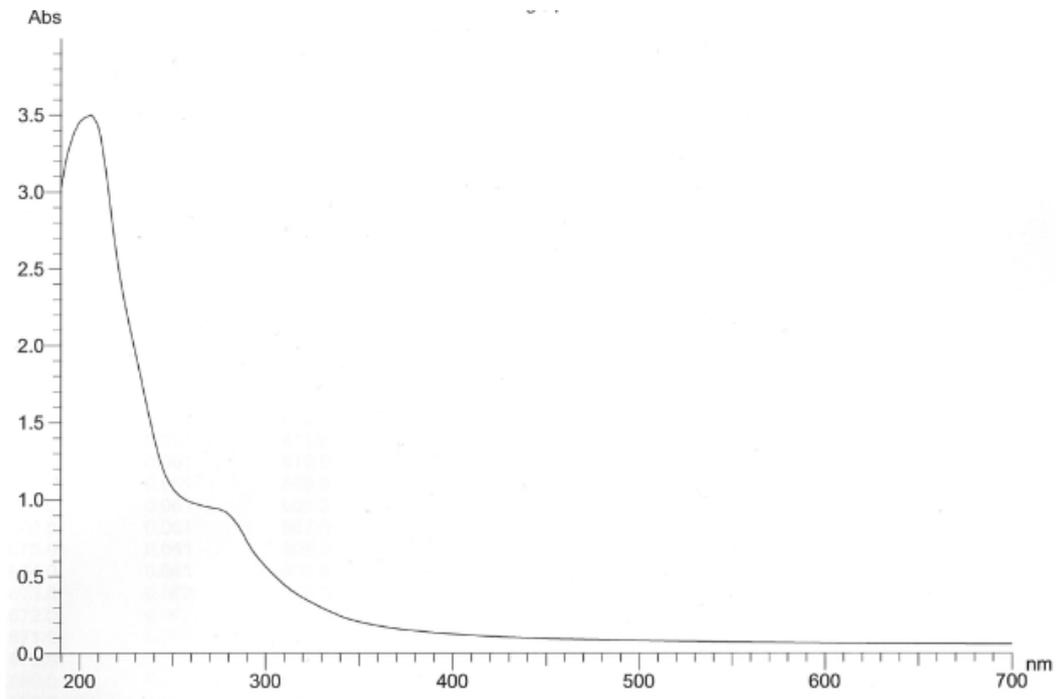
**Table III** PCD test results for wood handling stream.

<b>Parameter, mg/L</b>	<b>Ref 0</b>	<b>PCD 0.5</b>	<b>PCD 1</b>	<b>PCD 3</b>	<b>PCD 6</b>	<b>PCD 10</b>
<b>COD<sub>Cr</sub></b>	3450	3645	3550	3150	3100	3060
<b>BOD<sub>7</sub></b>	1850	1780	1720	1700	1760	1190
<b>Calculated BOD<sub>5</sub> (factor 0.93)</b>	1720	1660	1600	1580	1640	1110
<b>TOC</b>	1151	1186	1249	1203	1247	1237
<b>Cellobiose, HPLC-RI 2</b>	46.2	51.9	50.7	50.2	48.2	45.5
<b>Glucose, HPLC-RI 2</b>	219.8	233.5	238.8	239.8	235.8	231.3
<b>Xylose, HPLC-RI 2</b>	9.3	6.0	7.1	9.7	7.9	8.0
<b>Arabinose, HPLC-RI 2</b>	35.9	41.1	39.4	37.2	41.2	43.4
<b>Galactose, HPLC-RI 2</b>	8.7	8.0	9.2	11.2	10.7	10.6
<b>Mannose, HPLC-RI 2</b>	<5	<5	<5	<5	<5	<5
<b>Fructose, HPLC-RI 2</b>	267.6	266.5	262.8	252.3	245.3	233.8
<b>Carbohydrates total, HPLC-RI 2</b>	541.2	555.0	557.2	550.0	540.7	527.0
<b>Oxalic acid, PDA</b>	<5	<5	<5	18.9	46.6	80.2
<b>Citric acid, PDA</b>	43.1	50.4	60.5	24.4	40.4	43.4
<b>Succinic acid, PDA</b>	<5	<5	<5	<5	<5	<5
<b>Formic acid, PDA</b>	<5	<5	<5	48.7	71.6	104.6
<b>Acetic acid, PDA</b>	430.9	538.3	468.8	101.1	85.7	90.6
<b>Levulinic acid, PDA</b>	313.6	325.9	283.6	<5	<5	<5
<b>Carboxylic acids, total, PDA</b>	787.6	914.6	812.9	174.2	197.7	238.6
<b>2-Furoic acid, PDA</b>	<5	<5	<5	<5	<5	<5
<b>5-HMF, PDA</b>	<5	<5	<5	<5	<5	<5
<b>Furfural, PDA</b>	<5	<5	<5	<5	<5	<5
<b>Furans, total, PDA</b>	0.0	0.0	0.0	0.0	0.0	0.0
<b>Lignin, soluble, UV 205</b>	636	516	449	337	315	307
<b>Fatty acids, MTBE+GC</b>	0.7	0.5	0.6	0.5		0.5
<b>Resin acids, MTBE+GC</b>	0.3	0.3	0.1	<0.10		<0.10
<b>Sterols, MTBE+GC</b>	0.7	0.5	0.4	<0.10		<0.10
<b>Betulinols, MTBE+GC</b>	<0.10	<0.10	<0.10	<0.10		<0.10
<b>Steryl esters, MTBE+GC</b>	1.9	1.7	1.4	0.5		<0.10
<b>Triglycerides, MTBE+GC</b>	0.2	0.2	0.3	0.1		0.1
<b>Extractives, total, MTBE+GC</b>	3.8	3.2	2.8	1.1		0.6
<b>Lignans, MTBE+GC</b>	4	2	1	0		<0,10

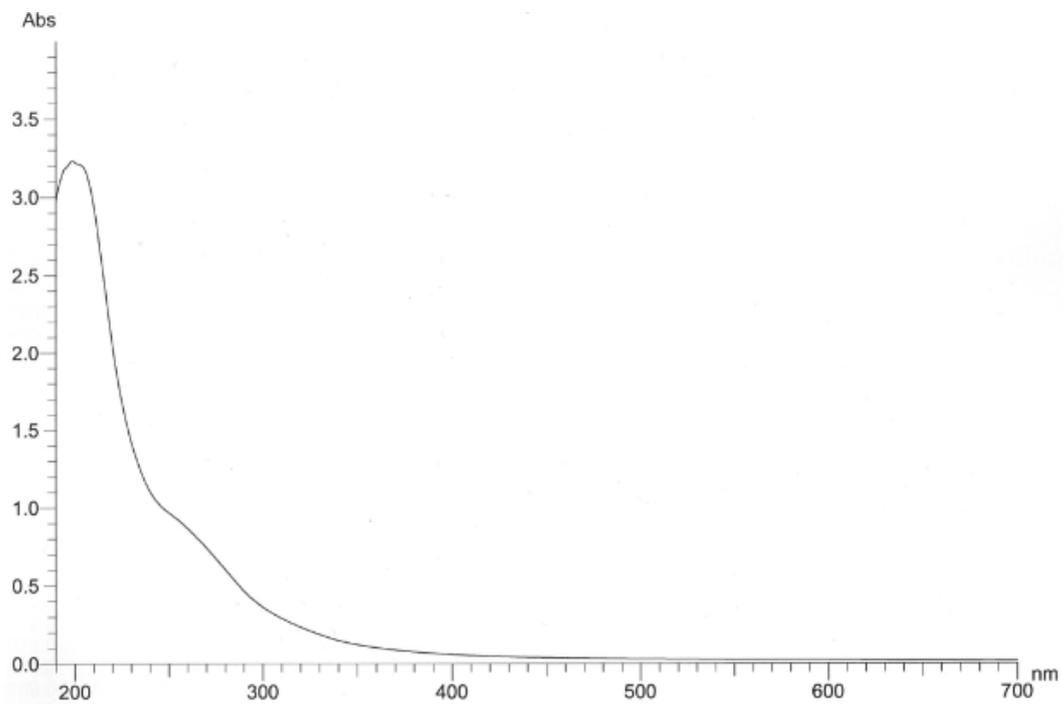
**Table IV** PCD test results for diluted ash containing stream.

Parameter, mg/L	Ref 0	PCD 0.25	PCD 0.5	PCD 1.5	PCD 3	PCD 5	PCD 8
<b>COD<sub>Cr</sub></b>	3610	3590	3540	3540	3390	3335	3240
<b>BOD<sub>7</sub></b>	1030	1000	980	960	930	920	1010
<b>Calculated BOD<sub>5</sub> (factor 0.8)</b>	845	820	804	787	763	754	828
<b>TOC</b>	1370	1330	1300	1270	1250	1290	1250
<b>Cellobiose, HPLC-RI 2</b>	<5	<5	<5	<5	<5	<5	<5
<b>Glucose, HPLC-RI 2</b>	277.2	268.3	276.3	135.6	110.5	53.4	104.0
<b>Xylose, HPLC-RI 2</b>	45.1	38.7	50.9	30.7	30.2	28.9	24.9
<b>Arabinose, HPLC-RI 2</b>	24.8	34.1	31.1	26.1	30.1	24.6	23.9
<b>Galactose, HPLC-RI 2</b>	57.7	64.9	66.8	64.3	65.6	59.6	62.3
<b>Mannose, HPLC-RI 2</b>	18.0	39.1	35.4	27.1	37.3	22.9	19.6
<b>Fructose, HPLC-RI 2</b>	120.6	136.0	133.6	113.0	143.5	88.6	95.3
<b>Carbohydrates total, HPLC-RI 2</b>	543.4	581.0	593.9	396.6	417.1	277.9	329.8
<b>Oxalic acid, PDA</b>	15.0	16.0	18.8	25.3	33.5	33.5	50.3
<b>Citric acid, PDA</b>	<5	<5	<5	<5	<5	<5	<5
<b>Succinic acid, PDA</b>	75.9	68.9	31.3	58.1	33.5	31.7	33.8
<b>Formic acid, PDA</b>	72.6	73.0	67.4	77.2	80.2	54.0	79.4
<b>Acetic acid, PDA</b>	<5	<5	<5	<5	<5	<5	<5
<b>Levulinic acid, PDA</b>	<5	<5	<5	<5	<5	<5	<5
<b>Carboxylic acids, total, PDA</b>	148.5	141.9	98.7	135.3	113.6	85.7	113.2
<b>2-Furoic acid, PDA</b>	<5	<5	<5	<5	<5	<5	<5
<b>5-HMF, PDA</b>	<5	<5	<5	<5	<5	<5	<5
<b>Furfural, PDA</b>	<5	<5	<5	<5	<5	<5	<5
<b>Furans, total, PDA</b>	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<b>Lignin, soluble, UV 205</b>	2395	3168	1436	1327	1150	1041	843

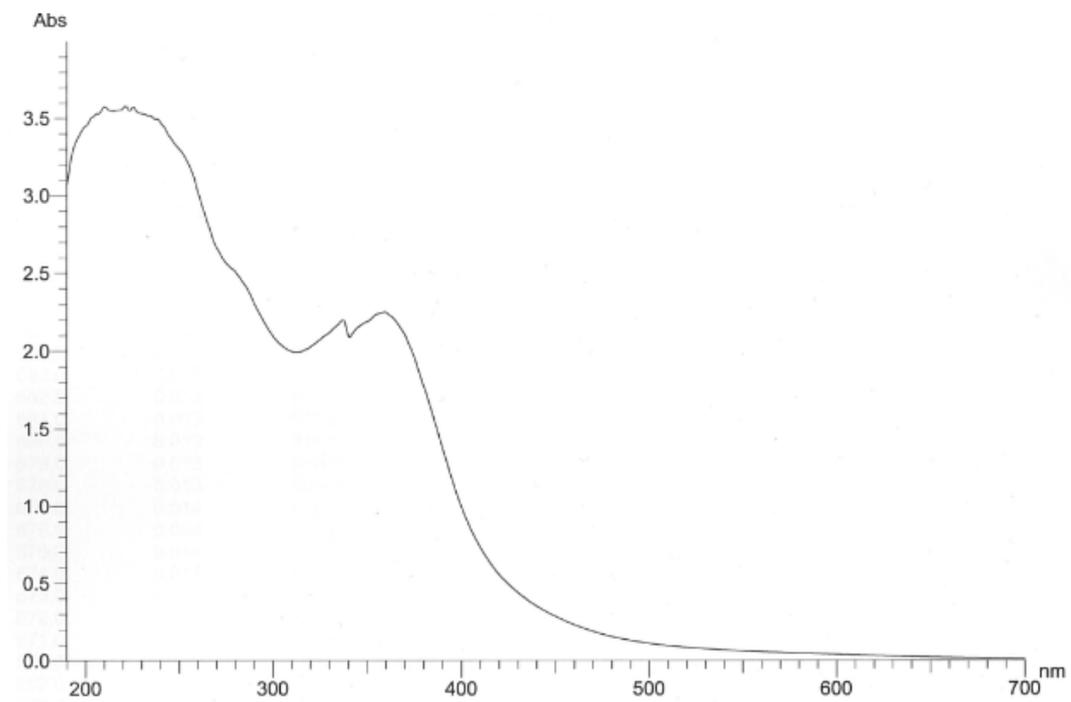
**Figure 4** UV-Vis spectrum from wood handling stream reference, dilution 1:10.



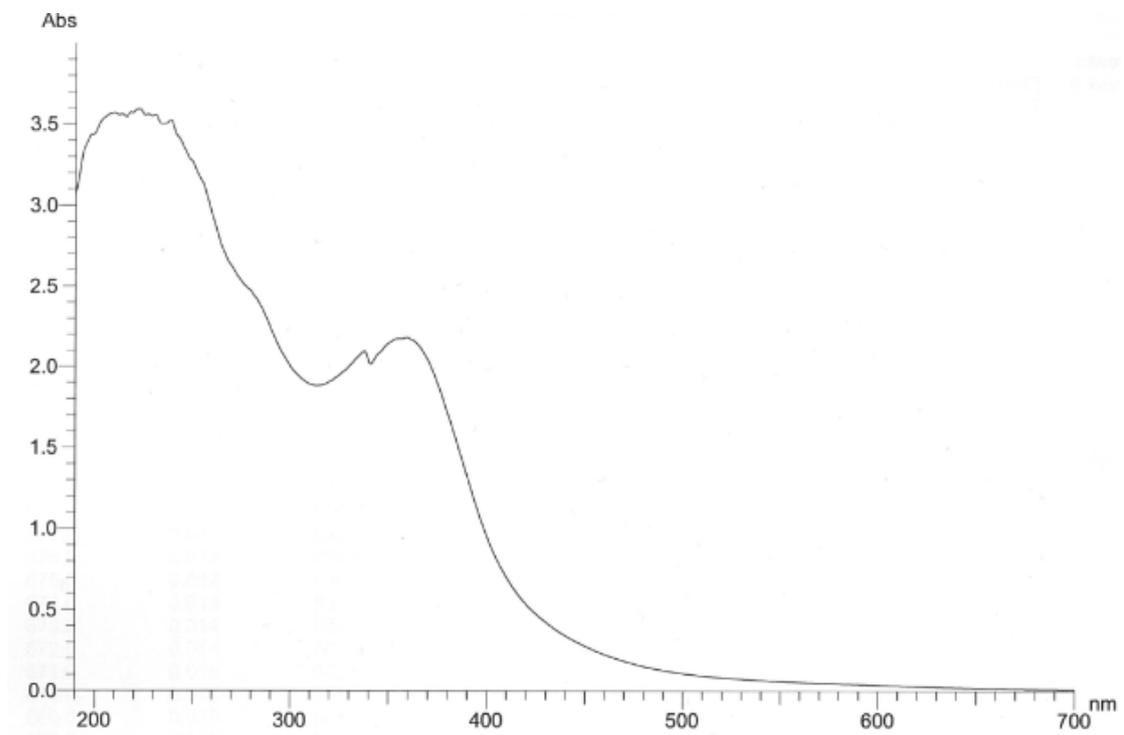
**Figure 5** UV-Vis spectrum from wood handling stream PCD 1 kWh/m<sup>3</sup>, dilution 1:10.



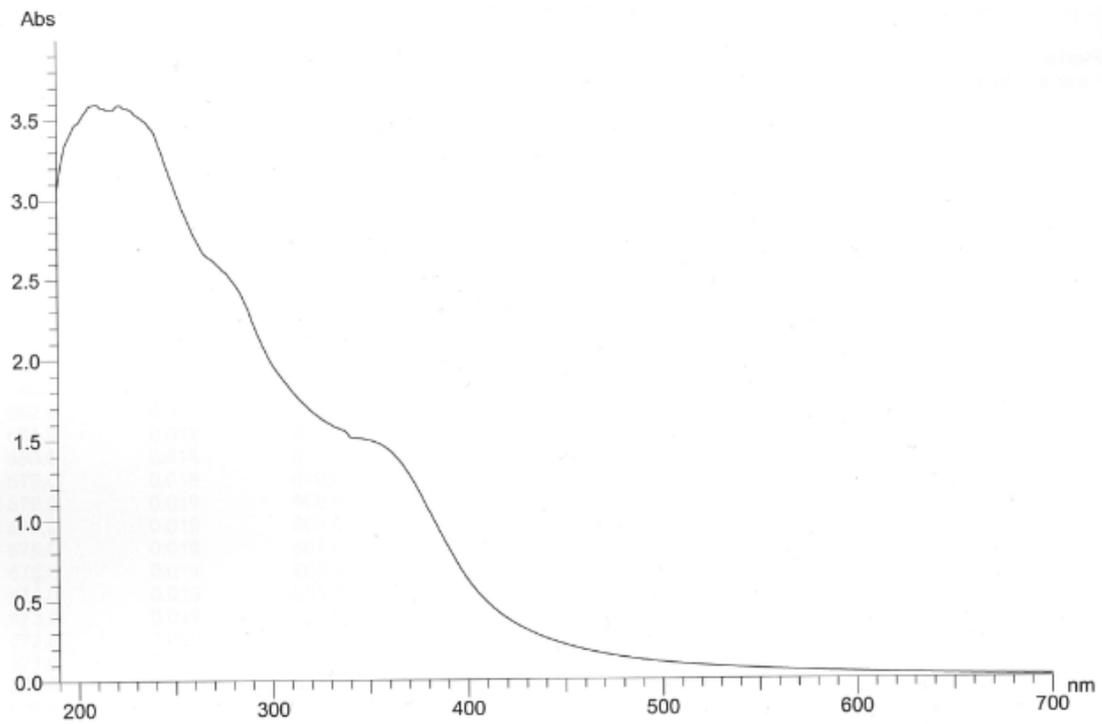
**Figure 6** UV-Vis spectrum from wood handling stream PCD 6 kWh/m<sup>3</sup>, dilution 1:10.



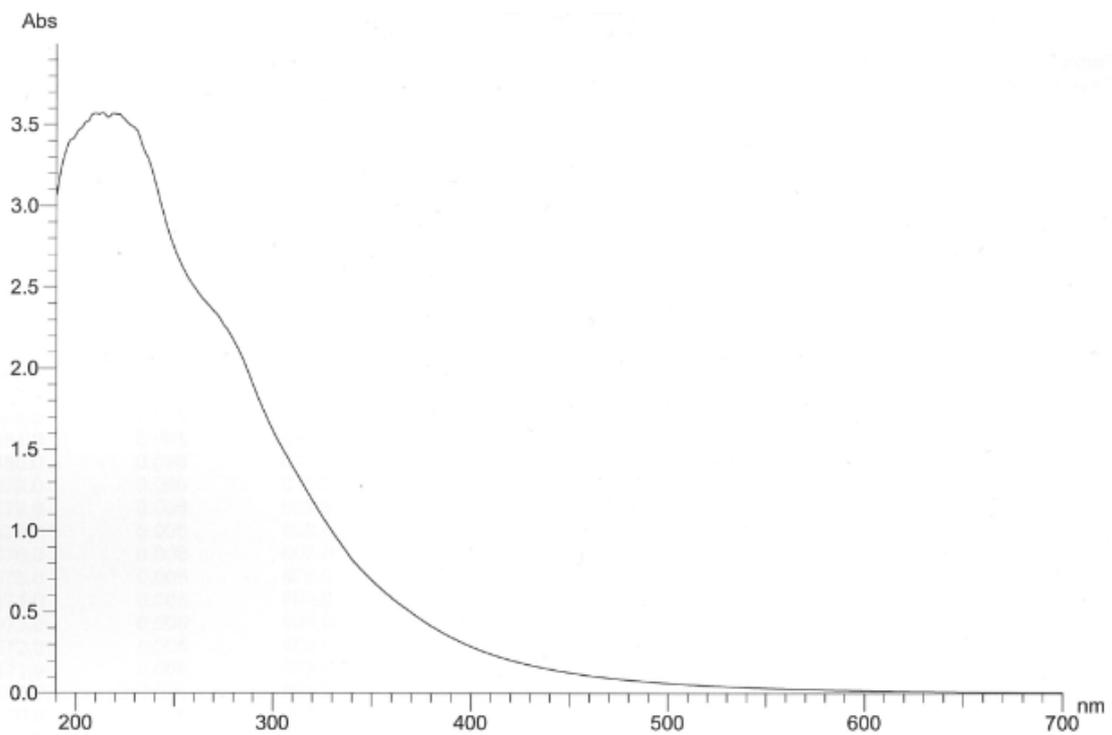
**Figure 7** UV-Vis spectrum from diluted ash containing stream reference, dilution 1:10.



**Figure 8** UV-Vis spectrum from diluted ash containing stream PCD 1.5 kWh/m<sup>3</sup>, dilution 1:10.



**Figure 9** UV-Vis spectrum from diluted ash containing stream PCD 3 kWh/m<sup>3</sup>, dilution 1:10.



**Figure 10** UV-Vis spectrum from diluted ash containing stream PCD 8 kWh/m<sup>3</sup>, dilution 1:10.